PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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Annual Report

PROJECT NO. A-204

Engineering Experiment Station
Georgia Institute of Technology
Atlanta
1955 - 1956

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 1

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

by

J. D. Walton, H. V. Grubb and R. B. Belser

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Contract No. NObs 66521
Index No. NS-061-087
Bureau of Ships, Code 1734F
Department of the Navy

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28 February 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 1

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

by

J. D. Walton, H. V. Grubb and R. B. Belser

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Contract No. NObs 66521
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Department of the Navy

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28 February 1955

I. SUMMARY

Conferences have been held with Ferro Corporation, Armco Steel Corporation and with International Nickel Laboratories.

A literature review has been started, and a compilation of the bibliography is about 90 per cent complete. A punched-card system has been devised to codify the information.

Frits and AISI C-1010 steel, as used by the Ferro Corporation in establishing the Thermal Shock Test, have been ordered. Low-hydrogen welding rods have been secured. A preliminary list of AISI steels for studying plate materials has been compiled.

Work has begun on a study of bonding behavior.

Laboratory rearrangements have been completed. A request for approval of the purchase of the furnace required for enameling was forwarded to the Bureau of Ships on 2 February 1955.

During the next month, work will continue on the T-joint thermal shock and acid-resistance qualifying test utilizing a furnace in the School of Ceramic Engineering, which is available for preliminary experiments. Preliminary tests will be conducted with nickel and other transition elements sputtered on enamel substrates. Plate materials in the range of AISI C-1006 through C-1038 will be ordered.

II. INTRODUCTION

Department of the Navy, Bureau of Ships, Contract No. NObs 66521 for research on "Porcelain Enameling Quality Steel Plates and Weldments" carries the initiation date of 15 January 1955. This project has been assigned as Project No. A-204 of the Engineering Experiment Station, Georgia Institute of Technology, and project work started on 1 February 1955.

Paragraph numbers shown in parentheses in the body of this report refer to the similarly numbered paragraphs in Specification SHIPS-P-1709 dated 1 October 1954.

III. EXPERIMENTAL PROGRESS

A. Preliminary Program

In order to obtain first hand the background knowledge of the Ferro Corporation who developed the T-joint thermal shock test and to obtain advice regarding sources of materials, guidance on techniques and so on, conferences were held with Ferro Corporation, Cleveland, Ohio; Armco Steel Corporation, Middletown, Ohio; and International Nickel Laboratories, Bayonne, New Jersey.

B. Coatings -- Qualifying Test (Para. 3.4)

The frits used by Ferro in establishing the T-joint thermal shock test were ordered along with suitable ground-coat frits. AISI C-1010 steel plate, also used by Ferro, was ordered.

A low-hydrogen welding rod was suggested by Armco and has been secured.

C. Literature Review (Para. 3.5)

As of March 1, the compilation of the bibliography was about 95 per cent complete. The references which were not available in the Georgia Tech Library have been ordered, and a code has been designed for using punched cards to codify the literature information. The reading of pertinent publications will be commenced immediately.

D. Plate Materials

A tentative list of steels based on carbon content and following AISI steel designations has been compiled. First samples to be procured will cover the range of C-1006 through C-1038 with all variables other than carbon kept as constant as possible.

E. Bonding Behavior

Work has begun on measurement of films deposited by sputtering on substrates of enamel. As a preliminary test, nickel was sputtered on an enameled surface and found to adhere to such a degree that a tensile stress of 1,500 psi did not cause failure. An investigation of the adherence of all of the transition metals, including iron, to various substrates composed of enamels is planned.

F. Facilities

Space and electrical facilities have been provided for the large furnace which is to be used for the enameling phase of this contract. Equipment has been installed to provide dry air for this furnace in order to minimize defects derived from moisture present in the furnace atmosphere.

IV. FUTURE PROGRAM

Steel plate covering the range of C-1006 through C-1038 will be ordered immediately.

Work on the literature review and on the bonding behavior of nickel and other transition elements will continue.

Upon receipt of the C-1010 steel on order, T-joint specimens will be fabricated. Surface preparation will be effected by burning at 1000° - 1500° F following with sand blast, light pickle and nickel flash. Arrangements have been made with the School of Ceramic Engineering for firing of the T-joint sections in their enameling furnace. The controls and availability of this furnace are not suitable for the experimental program but should be satisfactory for use in the qualifying test.

Detailed planning of the experimental program will continue and materials will be ordered as soon as possible.

Respectfully submitted:

J. D. Walton
Project Director

H. V. Grubb
Research Associate

R. B. Belser
Research Physicist

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 2

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL

PLATES AND WELDMENTS

by

J. D. Walton, H. V. Grubb and R. B. Belser

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31 March 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 2

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

by

J. D. Walton, H. V. Grubb and R. B. Belser

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31 March 1955

When sand blast alone was used to prepare the specimens after annealing, severe fish scaling resulted in the 3/16 in. plate. This condition was completely eliminated when the above-mentioned schedule was used.

At the present time, no "T" sections have been coated which pass the 5-cycle thermal shock treatment from 800° F (MIL-P-16961-B). However, most difficulty has been encountered with the 3/16 in. plate section rather than the 5/8 in. section.

The ground coat and cover coat used are those recommended by the Ferro Corporation specifically for this purpose.

Work is continuing in an attempt to comply successfully with the thermal shock test of paragraph 4.5.1.1 and 4.5.2.1 of MIL-P-16961-B. Concurrently work will begin in qualifying for the spray thermal shock test and acid resistance test of MIL-P-17378.

III. LITERATURE SURVEY

As of April 1, 1955, the compilation of the bibliography was completed. Approximately 90 per cent of the pertinent references have been read for coding purposes. The remainder of these references have been on order for at least four weeks and should be available soon. A relatively detailed report of the fish-scaling phenomena has been undertaken and should be finished in approximately two weeks. Work has begun on the classification of all other named enamel defects in somewhat less detail.

IV. BONDING BEHAVIOR

The work done on bonding behavior has been in preparation for a systematic study of the effects of bonding oxides on the bond developed. The

order of magnitude of bond developed has reached the limit of the test equipment, and modifications are under way to rectify this situation.

Respectfully submitted:

for J. D. Walton
Project Director

H. V. Grubb
Research Associate

R. B. Belser
Research Physicist

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 3

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

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J. D. Walton

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30 April 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 3

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

by

J. D. Walton

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Contract No. NObs 66521
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Department of the Navy

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30 April 1955

I. SUMMARY

T-joint specimens of two grades of steel, C-1012 and 0.03 per cent carbon, have been coated, and their resistance to thermal shock determined. The thermal shock test of MIL-P-16961-B was successfully passed with the very-low-carbon-content steel specimen. Low-hydrogen welding electrodes were used.

During the next month, emphasis will be placed on the fabrication of T-joint specimens of as many steels of different carbon content as may be obtained.

Equipment will be assembled to study the effect of carbon content on the diffusivity of hydrogen through steel.

II. EXPERIMENTAL PROGRESS

The work done on NObs 66521 during the past month has resulted in the satisfactory completion of the T-joint thermal shock test of MIL-P-16961-B.

The first T-joint specimens were fabricated from AISI C-1012 steel. Fish scaling was observed on the 3/16 in. web, which was eliminated only after the specimen had been pickled and nickel dipped. Even after this treatment, the thermal shock resistance was not satisfactory.

A steel of very low carbon content (0.03) was used for the 3/16 in. part of the T-joint, with the resulting specimen being free of fish scaling and of sufficient thermal shock resistance to pass the thermal shock test of MIL-P-16961-B.

All welding was accomplished by the manual arc method using General Electric's low-hydrogen electrode W616A (AWS6016).

The fish scale observed when the C-1012 steel was coated was attributed to the injection of hydrogen into the steel from the water contained in the ground coat frit. In order to provide additional information as to the source of hydrogen, and the relative diffusivity of hydrogen through high and low-carbon steels, the following work is planned:

1. From as many sources as practical, milled slip, proven to be suitable for the T-joint thermal shock test, will be procured for use in coating C-1012 steel.

2. T-joint specimens, fabricated by our personnel, will be submitted for coating by those who shall provide the prepared slip. These specimens will be compared with those coated in our laboratory.

3. Apparatus will be constructed in order to study the effect of carbon content on the rate of diffusion of hydrogen through steel.

The following steels have been ordered in 5/8 in. and 3/16 in. thicknesses:

AISI	C-1008	C-1025
	C-1010	C-1030
	C-1015	C-1035
	C-1018	C-1040
	C-1020	

and TI-NAMEL

T-joint specimens will be fabricated from each grade of steel as it is received.

III. LITERATURE SURVEY

As of May 1, 1955, all of the available pertinent references had been appraised. The discussion of fish scaling was almost ready for final review and editing and the discussions of other defects were being written. It is anticipated that the sections on causes and prevention of defects will be begun within the next two weeks.

Respectfully submitted:

J. D. Walton
Project Director

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 4

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

by

J. D. Walton

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31 MAY 1955

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of the Georgia Institute of Technology
Atlanta, Georgia

Status Report No. 4

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

by

J. D. Walton

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Contract No. NObs 66521
Index No. NS-061-087
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31 MAY 1955

I. SUMMARY

Various ground-coat frits which have been proven successful in coating T-joint specimens have been ordered. Various steel thicknesses of given-composition, hot- and cold-rolled steel have also been ordered.

The apparatus for carrying out hydrogen diffusion studies has been assembled to the extent of the available equipment.

Future work will deal with evaluating the new coatings, coating steels of various carbon content, and studying the hydrogen diffusion properties of steel samples as they are received.

II. EXPERIMENTAL PROGRESS

In an effort to overcome the fish-scaling problem encountered when the ground coat presently used has been employed, several different mill-batch compositions have been ordered.

The fish scaling has been prevalent in the 3/16-inch thickness of AISI C1012 steel whether the source of steel was plate or strip, with smooth or pitted surface. No fish scaling has been observed in the 5/8-inch thickness, even when the carbon content was raised to 0.35 per cent. In order to determine if thickness was an important variable, an 8- by 4-inch piece of 5/8-inch-thick plate was cut into two 4-inch-square pieces. One piece was set up in a lathe and 1/32 inch of the face was taken off each side. The other piece was set up in the same manner and the face cut down equally from each side until a total thickness of 1/8 inch remained. Both pieces were normalized, sand blasted, and enameled. Fish scale developed on the 1/8-inch-thick piece while the 9/16-inch-thick piece was completely void of fish scale, thus illustrating the fact

that plate thickness is a significant variable from the standpoint of fish scaling. This effect will be further studied when the hydrogen diffusion apparatus is completed.

In order to incorporate the variable of surface treatment with thickness, hot-rolled steel and cold-rolled steel covering a wide range of thickness have been ordered so that their hydrogen diffusion properties may be determined.

It is anticipated that such studies will be extended to determine the effect of cold working as effected by shot peening on the hydrogen diffusion properties of hot-rolled steel plate.

To date none of the steel plates of various carbon contents have been received.

III. LITERATURE SURVEY

As of June 1955, the writing concerning a critique of porcelain enamel defects has progressed as follows:

(1) All named defects have been defined and the reported causes and remedies for these defects listed. A rough draft of this section has been typed and is ready for editing.

(2) The bibliography containing some 400 references is ready for checking. Typing of this section should be completed during the second week in June.

(3) The sections containing discussions concerning the base metal, the enamel, and metal and enamel processing as sources of defects are being written and should be completed by the end of the second week in June.

(4) The introduction, conclusions, and recommendations have been partially written. The writing should be completed by the end of the second week in June.

(5) The report should be edited and ready for review by the project director by the end of the third week in June, possibly considerably sooner.

Respectfully submitted:

J. D. Walton
Project Director

Approved:

Frederick Bellinger, Head
Chemical Sciences Division

Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 5

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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JUNE 30, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 5

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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JUNE 30, 1955

I. SUMMARY

The hydrogen diffusion apparatus has been completed and diffusion studies begun. An apparatus for determining extractable hydrogen in steel is in the process of being constructed.

A firing chamber has been constructed which will permit firing of T-joint specimens in controlled atmosphere and at the same time eliminate the necessity of a back-up plate to control the heating rate of the 3/16-inch flange of the specimen.

II. EXPERIMENTAL PROGRESS

The hydrogen diffusion apparatus was completed, and the initial phases of the diffusion studies have been started. This apparatus differs from that used by Bryant et al.[1] in that the diffused hydrogen is collected in a gas burette and measured at atmospheric pressure and temperature.

First attempts to diffuse hydrogen through 3/16-inch plate produced erratic results. Therefore, further experiments were performed using sheet iron samples cut from a single piece of stock. Results thus far obtained indicate much less reproducibility than was originally anticipated.

In order to determine the amount of extractable hydrogen in the steel as received, as well as that injected into the steel during firing, a suitable apparatus is being constructed. This apparatus consists of a bell jar fitted with a gas burette. The steel sample is placed in the jar and mercury is added until the specimen is covered. The rest of the jar, as well as the burette and leveling tube, is filled with butyl phthalate. The jar is attached to a stainless-

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1. Bryant, E. E., Sweo, B. J., Miller, G. E., and Simmons, M. L., "A Study of Fish Scaling Produced by Induction of Hydrogen into Enameled Iron." J. Amer. Ceram. Soc. 32, No. 7, 248-52 (1953).

steel plate with suitable gaskets, and the plate is heated until the mercury assumes a temperature of 170° C. The system is maintained at this temperature overnight and any hydrogen diffusing out of the steel is measured in the gas burette.

When firing T-joint sections, it has been the practice to back up the 3/16-inch flange with a 5/8-inch plate in order to equalize the heating of the flange and web of the T-joint. In order to keep the 5/8-inch plate away from the 3/16-inch flange, small pins extending about 1/8 inch through the plate served to hold the flange and the plate apart. These pins, however, left a mark on the flange where contact was made.

In order to eliminate the objectionable marks left by the back-up plate and at the same time keep the temperature differential between the web and the flange to a minimum during the firing cycle, a firing chamber was constructed. This chamber was fabricated from 12-gage Inconel and assumed the shape of a rectangular box, fitted with a cover of the same material. Three T-joint specimens suspended on Inconel bars supported by holes located in the sides of the chamber may be fired at one time. The rod extended through the hole in the center of the 5/8-inch web of the T-joint specimen.

The T-joint specimens were placed in the cool chamber, the cover placed over the box and the entire unit placed in the furnace at the desired firing temperature. This procedure has been found satisfactory with one exception, that is, the tendency to fish scale is increased considerably. This can be explained by assuming that the moisture content of the air in the enclosed chamber before entering the furnace is higher than that of the furnace atmosphere. Therefore, with a relatively closed system, the moisture in the chamber provides a source of more hydrogen than would normally be found in the furnace atmosphere.

Flexible stainless-steel tubing has been ordered which will be used to carry dried air, as well as other gases, to the firing chamber. With this system, it should be possible to study, very efficiently, the effect of various furnace atmospheres on the firing of porcelain enamel. The chamber can be filled with the desired atmosphere before heating if necessary, and then as the chamber is heated only a small flow of gas would be necessary to maintain the desired atmosphere.

Future plans include continued hydrogen diffusion studies, as well as hydrogen-extraction studies. Controlled atmosphere studies will be attempted upon receipt of the necessary tubing. T-joint fabrication of various grades of carbon steels is held up pending receipt of the steels.

III. LITERATURE SURVEY

As of the first of July 1955, the progress concerning the literature search and review is as follows:

(1) The bibliography of over 400 references has been completely prepared for reproduction.

(2) All material has been written; approximately 50 per cent of the written material has been reviewed and edited. A rough draft of the edited section has been prepared.

(3) The remaining portion of the written material should be reviewed and edited by the end of the first week in July. A rough draft of the report should be forwarded to the Project Director during the second week in July.

Approved:

Wyatt C. Whitley, Acting Head
Chemical Sciences Division

Respectfully submitted:

J. D. Walton
Project Director

Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

Report A-204

STATUS REPORT NO. 6

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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August 31, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 6

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
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August 31, 1955

I. SUMMARY

A ground-coat enamel has been developed with exceptionally good thermal shock resistance. With this coating, it was possible to pass the thermal shock tests when coating the currently used steel without the rigorous cleaning and firing techniques required with the previous coatings.

T-joint specimens of AISI C1012 steel were submitted for commercial enameling with a proven coating and were thermal shocked. A specimen with only a single coating satisfactorily passed all quenching cycles. However, a section which was given two coats failed to pass the 900° F quench.

II. EXPERIMENTAL PROGRESS

In order to have comparative T-joint specimens for evaluating the coatings applied in this laboratory, four T-joint samples were fabricated from AISI C1012 steel and submitted to a commercial enameling firm for coating with an enamel which had been proven satisfactory for coating mufflers. Two of the samples were sand blasted at Georgia Tech, whereas the other pair was sand blasted by the enameler. One of each pair was given a single coat of the proven ground coat and the remaining samples were given two coats of the same ground coat.

These T-joint specimens were fired without benefit of shrouding and exhibited no evident detrimental effects from this severe firing treatment. The two specimens which were sand blasted by the enameler were thermal shocked according to the schedule required in MIL-P-16961. The single coated sample satisfactorily passed all quenches. However, the specimen with two coats failed after the third quench at 900° F.

Since much difficulty had been encountered in attempting to secure a proven coating for passing the thermal shock test of MIL-P-16961 when using

AISI C1012 steel, it was decided that an effort would be made to develop a good thermal-shock-resistant coating. A commercial ground-coat blend of four frits was used as a starting point.

It was found that a mill addition of 20 per cent A-1 alumina (Al_2O_3) and 5 per cent feldspar together with a suitable clay and set-up salts provided a coating which was exceptionally resistant to thermal shock. When using this coating, it was not necessary to prefire or pickle the specimens before coating in order to eliminate fish scale. Nor was it necessary during firing to provide a back-up plate or use the firing chamber in order to eliminate thermal straining lines. This coating not only passed the required thermal-shocking schedule of MIL-P-16961, but was still apparently unaffected after an additional five cycles of quenching from a temperature of 1000° F. The thickness of coating tested according to the thermal shock specifications of MIL-P-16961 ranged from 6 to 20 mils in one and two coats. The 1000° F quenches were performed as an experimental test on a single coating of 6 mils thickness after it had passed all the quenches specified in MIL-P-16961.

III. LITERATURE SURVEY

Editing has been completed and the typing of plates is more than half completed. It is anticipated that printing and binding will be completed by the third week in September.

Respectfully submitted,

Jesse D. Walton, Jr.
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO.7

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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OCTOBER 31, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO.7

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

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J. D. WALTON

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OCTOBER 31, 1955

I. SUMMARY

The hydrogen extraction apparatus has been modified to allow for the evacuation of the mercury-iron system prior to heating the specimen. This has reduced the chances of air being trapped between the iron and the mercury and thus affecting the accuracy of the experiment. Further changes have been made in the design of the apparatus to increase the life of the component pieces and, thus, to allow a greater amount of data to be obtained without interruption for repair or replacement of equipment.

II. EXPERIMENTAL PROGRESS

Work during the past month was directed entirely toward improving the design and construction of the hydrogen extraction apparatus. This apparatus was described in Summary Report No. 1 and shown in Figure 7, page 13.

In order to eliminate as many variables as possible, it was decided that several changes should be made in the procedure previously described.

It was considered possible that the mercury, when placed in the apparatus to cover the steel specimen, might trap air between the specimen and the mercury itself. In order to minimize this possibility, it was decided that the bell jar containing the mercury and steel specimen would be evacuated prior to having the gas burette attached and the remainder of the system filled with butyl phthalate. This, however, necessitated a change in the design of the apparatus. The asbestos gasket used to seal the bell jar did not form a vacuum-tight seal. The first attempt to rectify this situation was to use a Pyrex pipe nipple fitted with a standard taper joint on one end and the other end left, as received, to fit a Teflon gasket designed for the pipe. This fitting was secured to the stainless-

steel base plate by means of a flange designed to secure Pyrex pipe fittings together. This modification provided the desired vacuum-tight seal.

After only a few runs with this apparatus, however, a crack developed in the base of the Pyrex pipe where maximum pressure was exerted by the flange on the pipe. It appeared probable that the welding of the standard taper joint onto the pipe joint, followed by annealing, reduced the strength of the flange end of the joint. This difficulty was finally overcome by constructing the bell-jar portion of the apparatus in two sections. The upper section was composed of a 1-inch Pyrex glass nipple with the standard taper joint welded to one end. This was permanently secured to a 2- by 1-inch reducer by means of flanges designed for that purpose. A seal between the two joints was effected by means of a Teflon gasket. The 2- by 1-inch reducer was then secured to the stainless-steel base plate and served to contain the steel specimen and mercury. Thus, the portion of the joint which must be sealed for each extraction did not require annealing and was not weakened as in the previous design.

In order to insure the steel specimen remaining in a vertical position within the mercury, three stainless-steel pins were silver soldered in the stainless-steel base plate. Two of these pins were symmetrically located on one side of the specimen, and the third pin was located on the other side of the specimen, equidistant from the other two. This setup eliminated the possibility of hydrogen being trapped under the specimen and thus not being collected and measured.

At this time, it appears that this final design lends itself well to continuous operation of multiple units and should provide a means of obtaining the desired data as to the hydrogen existing in steel and the source of such hydrogen and its relationship to the defect-producing properties of the steel.

Respectfully submitted:

Jesse D. Walton, Jr.
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

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STATUS REPORT NO. 8

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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DECEMBER 31, 1955

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 8

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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DECEMBER 31, 1955

I. SUMMARY

Initial adherence studies have begun and will be continued as soon as furnace facilities permit.

The large muffle furnace has been ordered, and delivery is expected about the middle of February.

Welding electrodes representing ten AWS grades from eight different manufacturers have been received or have been ordered. Steel strip for welding studies has been received.

II. EXPERIMENTAL PROGRESS

Adherence studies were begun with the adoption of the "stretch test" method described by J. E. Sams in Proceedings of the Fifth Annual Forum of the Porcelain Enamel Institute, 1940.

First tests were made by stretching the enameled 2- by 14- by 3/16-inch strip 4 per cent over a specified 3-inch test length. This elongation caused removal of a great portion of the coating and exposed approximately 50 per cent of the metal surface as determined by a PEI Adherence Meter. Stretching another specimen 6 per cent produced essentially the same results. However, opposite sides of the same strip did not provide the same adherence data. Strain lines formed patterns of adherent and nonadherent areas of such a nature as to make a representative determination of adherence impossible. These lines have been identified as Luders lines and are common in low-carbon hot-rolled steels.

Further study of firing time and temperature on adherence appeared advisable before establishing a standard test. However, this phase of the program was halted because of furnace failure.

The welding studies have begun with the procurement of as many electrodes specified for mild and low-alloy steels by as many manufacturers as possible. To date ten different AWS grades have been ordered from eight different manufacturers.

Since it appeared that one of the primary differences between given electrodes, as well as between manufacturers, was the electrode coating, tests are being undertaken to evaluate the coating. An aging chamber has been constructed in which electrodes will be stored under conditions of 100 per cent relative humidity at room temperature. The moisture absorption will be determined for each coating as related to time. Welded specimens will be prepared using each electrode with its coating in the dry and moist condition. Hydrogen extraction and adherence data and incidence of fish scale or other defect will be determined and tabulated against moisture content and electrode composition.

Respectfully submitted:

Jesse D. Walton, Jr.
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 9

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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APRIL 1, 1956

I. SUMMARY

The large muffle furnace has been received and installed.

Steels representing different methods and degrees of killing have been received, together with the specimens of hot and cold reduced steel produced from one piece of AISI C1012 plate.

Adherence studies have begun on specimens welded with the electrodes specified in Annual Report No. 1.

II. EXPERIMENTAL PROGRESS

The following steels have been received from United States Steel Corporation.

Thickness	Deoxidation Practice	Chemical Analysis C	Mn	P	S	Si	Cu	Al
.187	Al K	.05	.30	.015	.034	.015	.06	.039
.148	Si-Al K	.19	.72	.011	.031	.19	.04	.028
.165	Al-Semi K	.12	.45	.010	.031	.008	.06	.009
.187	Si-Semi K	.16	.38	.012	.030	.06	.05	.009
.187	Rimmed	.04	.37	.008	.030	.007	.10	.005

Although these analyses depart somewhat from the requested AISI C1010 grade, they were the best which could be obtained under the circumstances.

The steel which was hot and cold reduced at Armour Research Foundation has been received. Originally there were shipped to Armour 7 pieces of hot rolled steel, 0.160 by 4 by 24 inches and 1 piece of cold reduced steel 0.1256 by 4 by 24 inches, both sets from a single coil of steel of the following analysis.

C	Mn	P	S	Si	Cu	Ni	Cr
0.07	0.34	0.008	0.029	0.005	0.02	0.02	0.01

The cold reduced samples were further cold reduced to provide specimens of the following thickness: 0.105, 0.072, 0.060, 0.048, and 0.036 inch.

The hot rolled sample was further hot rolled to provide samples of the following thickness: 0.125, 0.105, 0.075, and 0.060 inch.

Welding of specimens for adherence and hydrogen extraction studies has begun, using the electrodes specified in Annual Report No. 1. The samples for hydrogen extraction studies were welded with electrodes which had been exposed

to 100 per cent relative humidity conditions for 5 days. These specimens were not ground smooth or enameled prior to having the hydrogen extracted from them. The samples for adherence studies were welded with electrodes not exposed to high humidity conditions. After welding, the welded area was ground smooth and the sample was sand blasted and enameled.

III. FUTURE WORK

Hydrogen extraction and adherence studies will be continued using all of the various steels now on hand, and wettability studies will begin concurrently with this work.

Respectfully submitted:

Jesse D. Walton, Jr.
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

C-204

STATUS REPORT NO. 10

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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May 1, 1956

I. SUMMARY

Preliminary data on the adherence of porcelain enamel over welded areas indicate that those electrodes selected for study thus far evaluated provide welds of equal adherence characteristics.

Hydrogen extraction data of welded specimens indicate that little or no hydrogen remained in the specimens after the welded specimens had cooled to room temperature.

Initial wettability studies have begun using welded specimens as the base metal.

II. EXPERIMENTAL PROGRESS

Welded specimens were prepared for adherence studies, sand blasted and enameled. Elongation was accomplished as described in Annual Report No. 1. The average adherence count as determined by a PEI adherence meter is shown in Table I. An accident which occurred with the testing machine has halted further studies pending receipt of a new dial gauge.

TABLE I

Electrode Manufacturer	AWS No.	H_2 Ext.	ADH Count+
Lincoln	6010	.05	
NCG	6010	Nil	87
Hobart	6011	.10	
Westinghouse	6012	.05	87
Hobart	6013	Nil	
NCG	6013	.10	
Airco	6016*	Nil	
Hobart	6027	Nil	
Hobart	7016*	Nil	
M&T	7016*	Nil	92
Marquette	10013	.25	
Lincoln	6016*	Nil	

*Low Hydrogen.

+169 = No adherence.
0 = Optimum adherence.

Hydrogen extraction data were obtained by the method described in Status Report No. 9. These data are reported in Table I.

Wettability tests have begun by using the dried, milled enamel as the test material. A pellet was formed by placing 4 grams of the dried enamel in a 3/4-inch drill bushing with a 3/4-inch punch, acting as a piston, inserted in the bottom of the bushing. A second punch was inserted from the top and a force of 4,000 pounds applied to the pistons, after which the pellet was removed.

A 2- by 2- by 3/16-inch sample of steel was cleaned by sand blasting, and the pellet placed in the center to form the test specimen. Specimens were placed in a furnace at 1560° F for 12½, 15, 17½ and 20 minutes. The diameter of the fused pellets after the firing times listed above were 2.4, 2.7, 3.05 and 3.35 cm respectively. Reproducibility between 5 specimens fired at 1560° F for 17½ minutes was found to be 3.0 ± 0.05 cm.

III. FUTURE WORK

Welded specimens will be prepared for wettability studies by cutting a 2-inch piece from the 12- by 2- by 3/16-inch strip formed by welding 2 pieces of 1- by 12- by 3/16-inch strips together. The pellet will be placed in the center of the square and after fusion the spreading of the fused pellet parallel with the weld will be compared with that across the weld in order to evaluate the wetting properties of the weld metal.

The lack of hydrogen being injected into the steel during welding, or remaining in the steel once injected into it, appears to be due to the rate of cooling of the welded piece. Photomicrographs of the weld metal show good grain growth, indicating slow cooling. It is anticipated that a condition of cooling more nearly approaching that of the production welding of large items may be simulated by welding the specimens in contact with a chilled copper block. Under this condition more gases should be entrapped thus allowing more critical evaluation of the welding electrodes. Such a copper block is being constructed and welding studies using this modification will begin in the next interval.

Respectfully submitted:

Jesse D. Walton, Jr.
Project Director

Approved:

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

A-204

STATUS REPORT NO. 11

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. Walton

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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JULY 1, 1956

I. INTRODUCTION

Due to the greatly decreased rate of effort expended on this project during the months of May and June, this report will serve to cover work carried out during both months.

II. SUMMARY

Wettability studies were carried out on welded specimens as described in Status Report No. 10. Some differences were found in the spread of the fused pellet across the weld and parallel to the weld.

Hydrogen extraction data on welded specimens welded in contact with a chilled copper block indicated that still very little hydrogen was injected into the steel during welding. However, when the welding was done with the piece submerged in flowing water, much hydrogen was injected into the steel.

A study of oxidation, wettability, adherence and carbon content indicated that adherence and oxidation were related and that oxidation varied with carbon content. Wettability did not seem to be affected by carbon content. Adherence appeared to be more variable when the carbon content of the steel was below .20 per cent than when above this value.

III. EXPERIMENTAL PROGRESS

Welded specimens were prepared for wettability studies as described under Future Work of Status Report 10 dated May 1, 1956.

Pellets of pressed frit were placed over the welded area in the center of these specimens and allowed to fuse onto the steel. Measurements of the spread of the pellet across the weld and along the weld were made. From these data no conclusions could be reached. Although differences in measurements across and along the weld were noted, these were not consistent and appeared to be within experimental limits.

Since essentially no hydrogen had been extracted from welded specimens after welding, it was decided that welding techniques would be altered. A water cooled copper block was constructed which was used to cool the specimens during welding. Photomicrographs of the weld metal deposited under such conditions indicated that the grain growth was much less well developed than when no chilling was used. Still essentially no hydrogen could be extracted from these specimens after welding. When the welding was done under flowing water, however, 2.3 ml of hydrogen was extracted. After again for 24 hours, a check specimen yielded 0.8 ml of H_2 and after 96 hours the value had dropped to 0.4 ml. In order to determine the effect of heating on the amount of hydrogen extracted, additional check specimens were prepared. These were subjected to the regular firing cycle, after the specified aging period, but with no enamel applied. For the 24 hour aging time 0.4 ml of H_2 was extracted and for 96 hours, 0.3 ml of H_2 was extracted.

In studying oxidation of steel, 2 by 2 by 3/16-inch specimens were subjected to 1560° F temperature for 20 minutes. After removal from the furnace, they were allowed to cool in a carbon dioxide atmosphere. The weight gained during this treatment was taken as the measure of oxidation.

The effect of carbon content was first studies. It was found that oxidation decreased with increasing carbon content.

Table I lists the values obtained. Also shown in Table I are the adherence index values for the carbon contents studied, and the average diameter of

TABLE I

Effect of Carbon Content on Oxidation, Adherence and Wettability

Carbon Pct.	Oxidation (gms/sq in)	Average Oxidation (gms/sq in)	Adherence Index	Average Diameter of Fused Pellet (cm)
0.07	0.0159 0.0143 0.0164	0.0155	59	2.83

TABLE I

Effect of Carbon Content on Oxidation, Adherence and Wettability

Carbon (Pct.)	Oxidation (gms/sq in)	Average Oxidation (gms/sq in)	Adherence Index	Average Diameter of Fused Pellet (cm)
0.13	0.0135 0.0147 0.0148	0.0143	51	2.91
0.19	0.0130 0.0133 0.0146	0.0136	49	2.98
0.27	0.0115 0.0124 0.0122	0.0120	43	2.91
0.36	0.0106 0.0108 0.0100	0.0105	35	2.88
0.44	0.0092 0.0087 0.0096	0.0092	29	2.85

the fused pellets used in determining wettability. From this table it can be seen that a relationship appeared to exist between carbon content and oxidizability and adherence, but not with wettability. It was interesting to note that when the carbon content was 0.19 and lower, a greater variation in oxidation values was obtained between samples than when the carbon content was higher in this value.

Respectfully submitted:

J. D. Walton
Project Director

Approved:

W. C. Whitley, Chief
Chemical Sciences Division

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 1

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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July 31, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 1

Project No. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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July 31, 1955

I. SUMMARY

Thermal shock test of MIL-P-16961B was passed when the steel used for the 3/16-inch web section contained 0.03 per cent C. Fish scaling resulted when the carbon content was increased to 0.12 per cent. No defects were encountered with the 5/8-inch flange although the carbon content of this component was 0.12 per cent throughout the tests.

Steels of carbon content ranging from 0.08 to 0.40 per cent have been ordered.

Hydrogen diffusion studies have revealed that cold working, such as sand blasting, decreases the diffusivity of hydrogen through steel. Samples have been submitted for shot peening to determine the effect of cold working on fish scaling.

Hydrogen extraction studies have indicated that moisutre in enamel frit and firing atmosphere is the most important source of hydrogen in enameled steel.

A firing chamber has been constructed which permits the firing of T-joint specimens in controlled atmospheres without the necessity of shrouding.

II. INTRODUCTION

This project was initiated on January 15, 1955 and has as its objectives:

a. to determine the factors which affect the enameling characteristics of steel Plates and Weldments.

b. to establish the validity of parameters and set limits for control of quality necessary for enamelability of steel Plates and Weldments.

c. to assess the factors responsible for defective coated parts intended to conform to Specification MIL-P-16961.

III. EXPERIMENTAL PROGRESS

In order to meet the qualification requirements of MIL-P-16961B and to become familiar with the enameling properties of steel as well as the enameling of steel plate, conferences were held with representatives of the following companies:

Ferro Corporation
Armco Steel Corporation
International Nickel Laboratories
A. O. Smith Corporation
The Pfaudler Company
Atlantic Steel Company
Inland Steel Company

As a result of these conferences, and acting upon their recommendations and suggestions, the following experimental program was carried out.

A. Thermal Shock Test

The steel selected for use in fabricating the T-joint specimens was AISI C1012, which was secured in the form of 4-by-3/16-inch strip and a 4-by-5/8-inch flat. The component pieces of the T-joint were assembled as shown in Figure 1. Welding was accomplished by the manual-arc method using a Miller AC welder at a voltage setting of 200V. The welding electrode used was General Electric's low-hydrogen electrode W-616A (AWS-6016) 5/32-inch D. Welding was first attempted using direct current, normal and reversed but excessive spattering and blow-back resulted. This tendency was reduced somewhat by using alternating current. The welding operation is illustrated in Figure 2.

The ground-coat and cover-coat frits selected for use were recommended specifically for the thermal shock test and were applied by spraying after the T-joints had been cleaned. Cleaning was accomplished by sand blasting after fabrication, burning at 1500°F for 30 minutes followed by a second sand blasting.

Figure 1. Assembly for Holding T-Joint for Welding.

Figure 2. Welding of T-Joint.

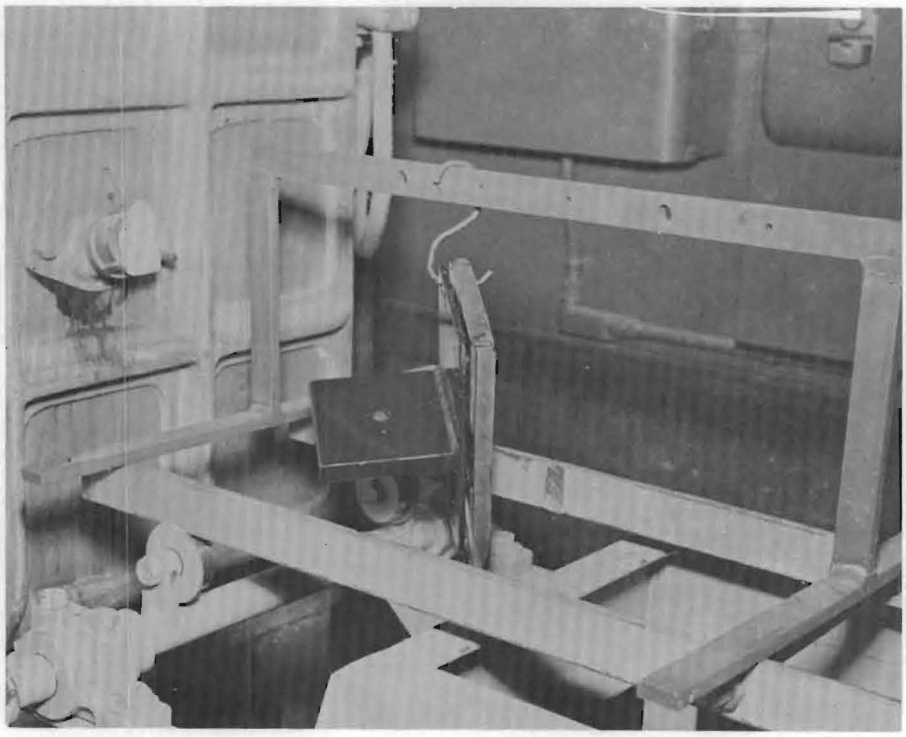

Figure 3. Firing Position for T-Joint with Shroud.

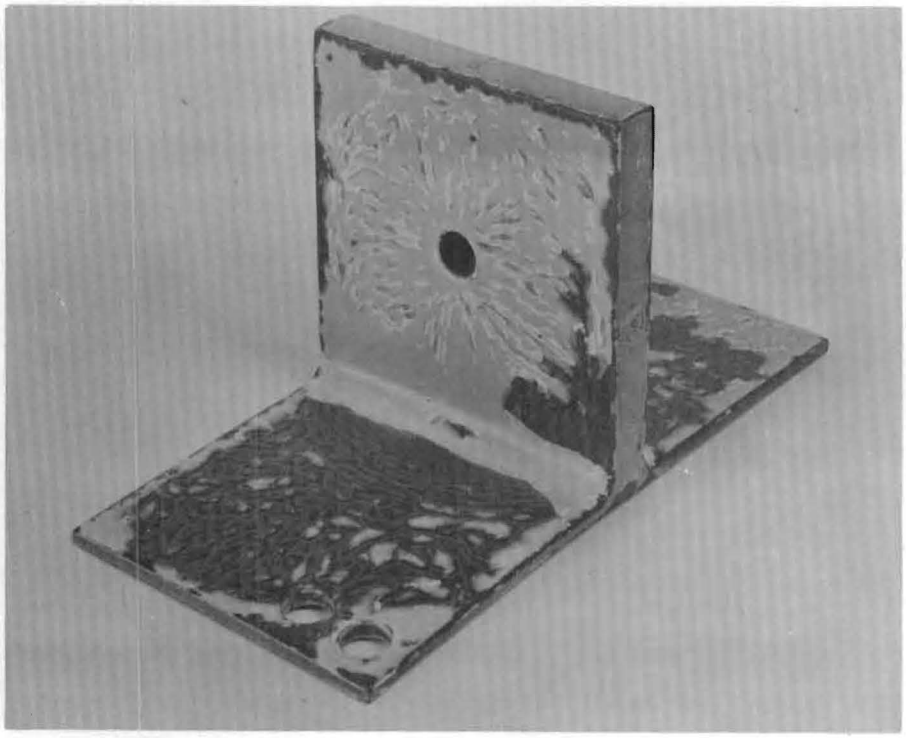

Figure 4. Underfired T-Joint After Thermal Shock.

In order to equalize the heating of the 5/8-inch flange and 3/16-inch web sections of the T-joint, a shroud was constructed to reduce the heating rate of the 3/16-inch web. A T-joint specimen in firing position with shroud is shown in Figure 3. The shroud was fabricated by welding two pieces of 4-by-3-by-5/8-inch plate together by means of two 1/4-by-1/2-inch pieces of strip iron to form a 4-by-8-inch rectangular section with a void of 4-by-2-inches in the center. This void was designed to be located behind the area of juncture of the web and flange, since the heating of this area of the web is sufficiently slow as to require no shrouding. In order to keep the shroud from touching the web section during firing, four screws were placed in the four corners of the shroud and extended through the shroud approximately 1/4-inch. The ends of the screws were ground to form small pins which served to separate the body of the shroud from the web.

A furnace, located in the School of Ceramic Engineering was used for firing these sections. First attempts at coating specimens met with no success due to under-firing which was traced to faulty control equipment. However, the under-fired sections served to illustrate one fact, that is, the presence of thermal strain lines, even though a shroud was used. These became quite evident after thermal shocking in coldwater from a temperature of 800°F. (See Figure 4.) These thermal strain lines were not evidenced in sections fired at the recommended temperatures and thermal shocked. Failures evidenced under these conditions were manifested in spalled areas, roughly circular in shape.

Throughout the previous coating of T-joint samples, fish scaling had been prevalent in the 3/16-inch web section. Other sources of AISI C1012 steel in the form of plate were tried, but to no avail. However, the 5/8-inch flange section of the T-joint never exhibited fish scaling although it too was of AISI C1012 steel.

One piece of 3/16-inch steel 8 inches by 4 feet was located with a carbon content of 0.03 per cent. This steel, when used as the web component of the T-joint, did not exhibit fish scaling, and when coated as the previous T-joint specimens were, satisfactorily passed the thermal-shock test.

It was still necessary, however, to find some method of preparing the surface of the C1012 steel in order to eliminate the fish scaling. This was finally accomplished through the use of pickling and nickel flash which followed the previously described cleaning technique. The cleaning schedule was 2 minutes in 6 per cent H_2SO_4 pickle solution at a temperature of 140-160° F, rinse, 5 minutes in a single nickel salt solution of 2 oz/gal maintained at 140-160° F and 5 minutes in a 0.1 per cent Na_2O neutralizer solution of sodium cyanide and meta silicate at 160-180° F. All pickling was done by a local enameling firm. Even though it was now possible to enamel the higher carbon web section without fish scale, these T-joints would not pass more than the 5 quenches from 800° F.

An enamel which was reported as having both excellent fish-scale resistance and thermal shock resistance was procured and tried. This enamel, however, fish scaled as badly as the other on the 3/16-inch sections.

Although steels of the desired carbon contents in the necessary thicknesses have not been received, four pieces of steel strip were used to demonstrate a difference in enamelability and thermal-shock resistance as related to carbon content. Two plates were made from these four pieces of steel strip. One plate was made by butt welding two pieces of 1/2-by-3-by-6-inch steel strip together to form a 1/2-by-6-by-6-inch plate. The carbon content of one of the component plates was 0.09 per cent and the other was 0.24 per cent. The

second test plate was fabricated in a similar manner except the plate thickness was 3/8-inch and the carbon content of the component pieces was 0.15 and 0.35 per cent.

During the cooling of these plates, after firing, it was observed that the lower carbon content strip of each plate cooled noticeably slower than the higher carbon component. After ground coating and cover coating, these plates were subjected to three quenches in cold water from 800°F. The lower carbon component of each plate exhibited large areas of spalling ranging from 3/8-inch diameter spalls to 4-by-1-inch spalled sections. However, the 0.24 per cent carbon piece exhibited only nine fish scales located along the outer edge of the piece, and the 0.35 per cent carbon piece exhibited only one isolated fish scale.

The welded areas of these plates, as well as the T-joint specimens thus far fabricated, have been significantly free of defects.

In order to evaluate the effect of plate thickness on fish scaling, an 8-by-4-inch piece of 5/8-inch thick plate was cut into two 4-inch-square pieces. One piece was set up in a lathe and 1/32-inch of the face was taken off each side. The other piece was set up in the same manner and the face cut down equally from each side until a total thickness of 1/8-inch remained. After coating, fish scale developed on the 1/8-inch-thick piece while the 9/16-inch-thick piece was completely void of fish scale.

At this point in the work, it was considered probable that either or both of two sources of hydrogen were responsible for the fish scaling. One was the furnace atmosphere, the other the frits themselves. In order to have some means of controlling the firing atmosphere, without the problem of replacing the furnace atmosphere, the firing chamber shown in Figure 5 was constructed.

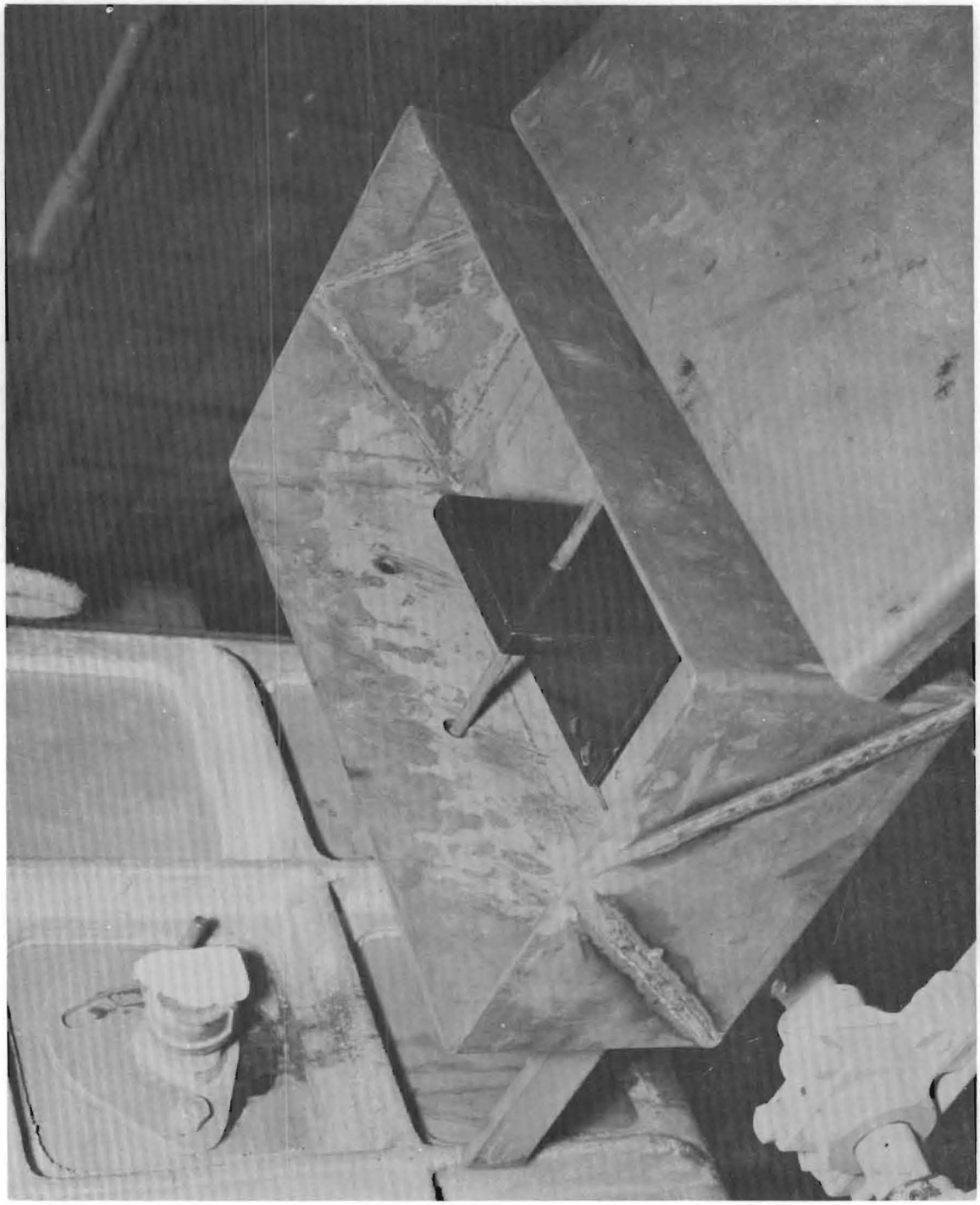

Figure 5. T-Joint in Firing Chamber.

This chamber was fabricated from 12 gauge inconel as was the cover, part of which is shown in the lower right hand corner. Three T-joints may be fired simultaneously, suspended as shown. By fitting this enclosure with appropriate tubing, any desired atmoshpere may be used to fill the chamber and this atmosphere can be maintained throughout the firing cycle.

This firing chamber serves one other function which is to replace the shroud previously required to retard the heating of the web section. By placing the T-joint specimens in the cold firing chamber and covering it and then placing the entire system in the furnace, remarkably uniform heating and cooling of the entire T-joint is obtained without the pin marks left on the back of the web as in the case of the shroud.

B. Hydrogen Studies

Since the most detrimental defect thus far encountered has been fish scale, which is reported to be a hydrogen defect, it was decided that equipment would be constructed to study the behavior of hydrogen in steel.

1. Hydrogen Diffusion

The apparatus shown in Figure 6 was constructed to diffuse hydrogen through steel. The diffusion cell is shown in the middle of the figure suspended just above the surface of the water in the constant temperature bath. The cell is divided into two compartments separated by the steel sample undergoing investigation. The left portion of the cell contains the electrolyte which is an 11 per cent solution of H_2SO_4 with 0.05 grams of As_2O_3/liter of solution. The sample plate acts as the cathode with a platinum anode extending into the opening of the electrolyte cell. The right portion of the cell contains butyl phthlate and is fitted with a gas burette and leveling bulb. A direct current generator is used to supply a potential between the platinum anode and

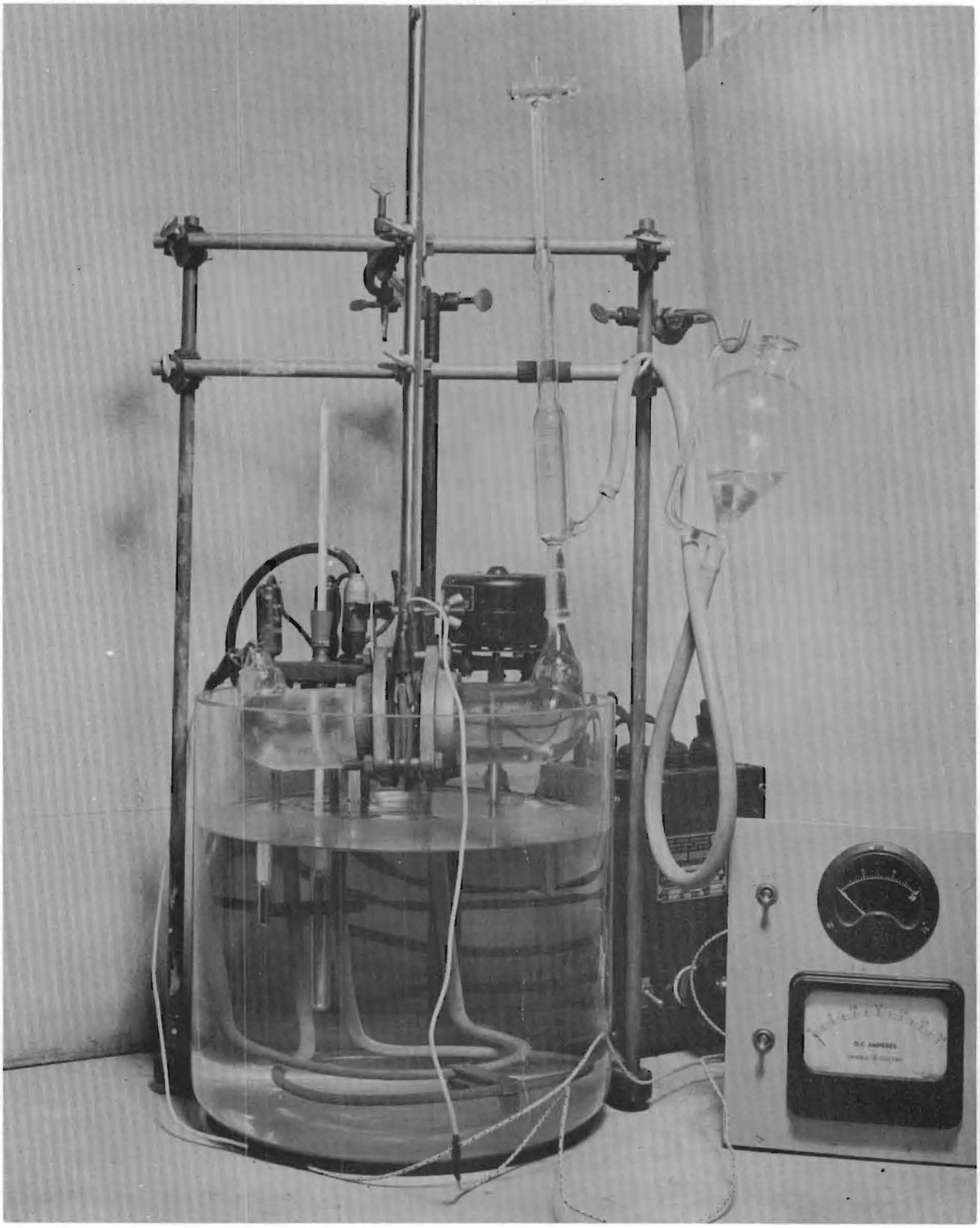

Figure 6. Hydrogen Diffusion Apparatus.

steel sample cathode which causes direct current to flow through the electrolyte. The body of the cell is kept at a constant temperature of 35° C through immersion in the water bath.

Hydrogen is formed at the face of the steel plate in contact with the electrolyte. Some atomic hydrogen, however, remains in the steel and passes through to form molecular or gaseous hydrogen in the butyl phthalate and is collected in the gas burette and measured under atmospheric conditions of temperature and pressure. This collected hydrogen is referred to as diffused hydrogen.

Since the only references in the literature to the diffusion of hydrogen through steel have dealt with sheet steel it was decided that first attempts to carry out such work would be done by using 18 gauge enameling iron.

Reproduceability between samples was found to be very poor unless comparable samples were cut adjacent to one another. All samples used were 3-by-4-inches. However, the area in contact with the electrolyte was π square inches, as determined by the 2-inch diameter of the cell opening. Two samples, A and Z, cut from opposite ends of a two foot strip whose length paralled the direction of rolling were set up in the diffusion apparatus. The average rate of diffusion of A was 0.02 ml/min in 100 minutes while Z was 0.03 ml/min over the same period. Sample B was then cut adjacent to A and Y next to Z with the average rate of diffusion for B being 0.023 ml/min and Z being 0.033 ml/min. This reproduceability was possible only when cleaning with a wire wheel was employed. Much greater discrepancy was observed when sand blasting was used as the method of cleaning. All of these test were carried out at a potential of 3.5 volts with 1 amp of current flowing. Lower voltage

appeared to improve reproduceability. However, at this point, it appeared that the effect of surface treatment should be studied and more attention given to diffusion studies using steel plate.

To evaluate the effect of sand blasting on the hydrogen diffusion properties of 18 gauge enameling iron, two samples were prepared by sand blasting. Sample 1 was sand blasted just enough to clean the surface, whereas sample 2 was sand blasted much more severely. As a result, 2.50 ml were diffused through sample 1 over a period of 150 minutes whereas only 1.15 ml were diffused through sample 2 over the same period of time. A repeat of this experiment produced values of 1.55 for the normally sand blasted piece and 0.05 for the excessively sand blasted piece, both over a period of 150 minutes. Although the values from individual heavily sand blasted pieces varied to a considerable extent, it was still thought that a significant difference was evidenced as a result of sand blasting.

In the case of sand blasting, only the very surface itself is cold worked. Therefore, it would not be expected that a great amount of grain reduction and peening would be realized through this method. For a more severe example of cold worked surface, samples of AISI C1012 plate, 3/16-inch thick which has exhibited fish scaling, have been submitted for various degrees of shot peening. The tendency of these specimens to fish scale will be related to the degree of surface cold working received.

2. Hydrogen Extraction

Since the hydrogen injected into the steel by any of several mechanisms appears to be the cause of fish scale, the apparatus shown in Figure 7 was constructed with which hydrogen could be extracted from steel. Thus the various reported sources of hydrogen could be evaluated and their relative importance determined.

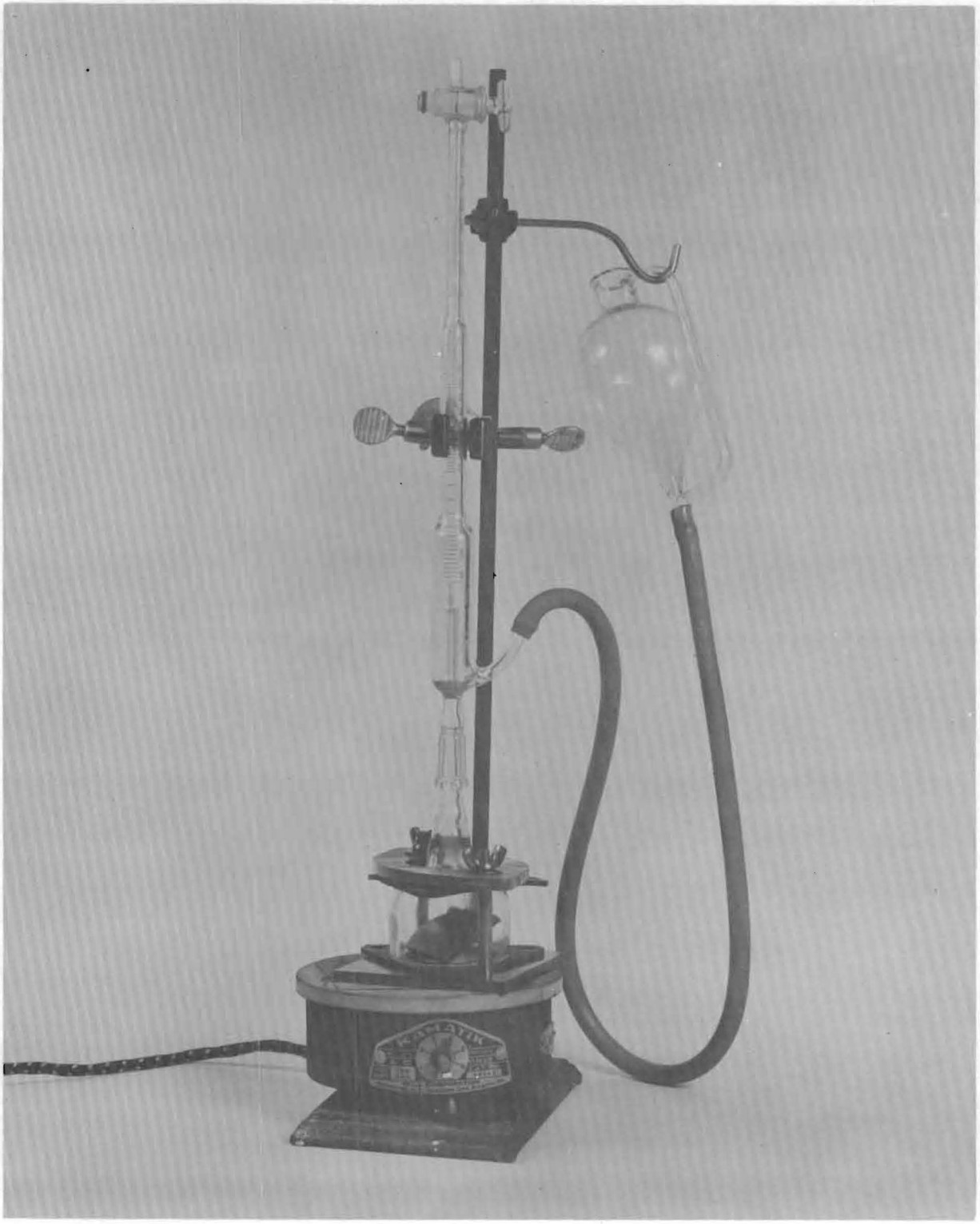

Figure 7. Hydrogen Extraction Apparatus.

The extraction chamber consists of a bell jar fitted with a standard taper joint. This jar is clamped to a stainless steel plate and a seal is effected by means of an asbestos gasket. To the top of jar is fitted a gas burette with leveling bulb.

A 1 1/2-by-2-inch steel sample is placed in the jar and mercury added until the sample is submerged. Butyl phthalate is then added to cover the mercury and fill the gas burette. The system is then placed on a hot plate which is adjusted to maintain a mercury temperature of 170° C. The system is then left overnight and the hydrogen collected during this period is reported as extractable hydrogen.

A 1 1/2-by-2-inch piece of 3/16-inch plate, placed in the apparatus as previously described, liberated only one small bubble of gas over night. This amounts to only a fraction of the first division on the burette which is 0.05 ml. The same amount was extracted when a similar piece was heated at 1560° F for 15 minutes and cleaned with a wire wheel. When the same steel was coated with the ground coat used for coating the T-joint specimens and heated in the extraction apparatus over night, 0.14 ml of gas was liberated and the piece exhibited fish scale.

In order to investigate another of the reported causes of fish scale, a piece of the same steel was treated as above except that during the firing of the coating, air, passing through boiling water, was injected into the furnace. This piece liberated 0.82 mls of gas and was severely fish scaled.

A study was next carried out of the effect of a moist atmosphere on the uncoated steel when heated to firing temperatures. Under the same condition as the previous test, but without a coating on the steel, it was found that

again only a small bubble of gas was liberated. However, when a similar piece was put in the furnace, lying upon a wet refractory pallet with water continuously dropped on the surface of the specimen throught the heating cycle, a total of 0.55 ml of gas was extracted.

The importance of acid pickling as a source of hydrogen was touched upon by immersing a test specimen in a 6 per cent H_2SO_4 solution at 175° F for a period of ten minutes. The gas extracted after this treatment was 0.14 ml.

A piece of steel plate which had had hydrogen diffused through it in the hydrogen-diffusion apparatus was set up in the extraction apparatus. A volume of 1.54 ml of hydrogen was extracted. It might be assumed in this instance that the steel was saturated with hydrogen. Thus in the case of the enameled piece, fired in a moist atmosphere, more than 50 per cent saturation with hydrogen was obtained.

IV. THERORETICAL CONSIDERATIONS

In light of the results of the work to date, it appears that the frit and the firing atmosphere are the primary contributing factors to inducing hydrogen into steel.

First, it appears that moisture in the atmosphere does not contribute significant amounts of hydrogen into steel through the reaction of

$$H_2O + Fe \longrightarrow FeO + H_2 \qquad (1)$$

since the amount of such hydrogen was insignificant except in the presence of actual flowing water.

Second, equilibrium data reveal that the amount of atomic hydrogen produced through the dissociation of molecular hydrogen at firing temperatures

is infinitesimally small even in an atmosphere of pure hydrogen gas. Thus it appears that the moisture in the atmosphere must contribute its influence as H_2O.

In considering moisture in the frit, however, a more available source of atomic hydrogen comes to light.

First, the presence of moisture at the interface is in direct contact with the metal. Thus a greater chance for hydrogen to result from the reaction shown in Formula 1.

Second, one of the mechanisms by which adherence is achieved is reported to be the electrochemical replacement of cobalt from glass solution with iron being taken into solution. This reaction would promote the electrolysis of water at the areas in which this cell action was active, creating atomic hydrogen.

If these actions are responsible for the majority of hydrogen injected into steel during the firing operation, the amount of hydrogen would then be proportional to the amount of water present in the frit in equilibrium with the moisture in the furnace atmosphere.

With respect to means of preventing fish scale, it would appear that elimination of moisture from the frit and the atmosphere would prove the most successful remedy. However, this is not easily accomplished in practice, thus other means would seem desirable. One such method is evident from the hydrogen diffusion studies, and this is the cold working of the metal surface prior to coating. This cold worked surface provides areas of metal discontinuities at broken grain boundaries. These areas do not tend to stop the passage of atomic hydrogen being injected into the steel during the firing operation. However, upon the diffusion of hydrogen from the steel at room

temperatures, molecular hydrogen is formed in the voids or areas of discontinuities and further diffusion is stopped. If the hydrogen can thus be prevented from entering voids produced at the enamel-metal interface resulting from undissolved oxide or poor wetting of the metal surface, fish scaling can be reduced. Other remedies such as improved bubble structure to better distribute the diffused hydrogen pressure over large areas may be considered.

V. BIBLIOGRAPHY

The bibliography has been completed and the discussion is in the final stages of preparation. It is estimated that it will be ready for transmittal to the Bureau of Ships during the month of August.

VI. FUTURE WORK

Work presently planned includes the thermal shocking of T-joint specimens fabricated from the following grades of AISI steel:

C1008	C1025
C1010	C1030
C1015	C1035
C1018	C1040
C1020	

These steels have been on order for some time and their delivery is anticipated momentarily.

The shot peened samples of AISI C1012 steel will be coated to determine susceptibility to fish scaling. Microscopic examinations will be made to determine the degree of cold working and its effect on bubble structure. These data will be correlated with hydrogen diffusion and extraction data.

Controlled atmosphere firing will begin with receipt of necessary flexible stainless steel tubing for carrying the desired gases to the firing chamber.

Such atmospheres as dried air, carbon dioxide, hydrogen and helium will be studied. The effect of these atmospheres on adherence, bubble structure and fish scaling will be determined.

Respectfully submitted:

J. D. Walton, Jr.
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 2

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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September 30, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 2

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
BUREAU OF SHIPS, CODE 1734F
DEPARTMENT OF THE NAVY

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September 30, 1955

I. SUMMARY

A ground-coat enamel has been developed which exhibits excellent thermal-shock resistance. This coating, when applied to a T-joint specimen, fabricated of AISI C1012, not only successfully passed the thermal-shock schedule of MIL-P-16961 but withstood an additional five quenches from 1000° F without failure.

A test has been developed to determine the amount of hydrogen injected into a steel specimen when porcelain enameled.

Arrangements have been made for reducing the thickness of a steel sample, by both hot and cold methods, so that the method of reduction may be compared with the enameling quality of the steel.

II. INTRODUCTION

This project was initiated on January 15, 1955, and has as its objectives:

1. To determine the factors which affect the enameling characteristics of steel plates and weldments.

2. To establish the validity of parameters and set limits for control of quality necessary for enamelability of steel plates and weldments.

3. To assess the factors responsible for defective coated parts intended to conform to specification MIL-P-16961.

This summary report covers the period of July 31 through September 30, 1955.

III. EXPERIMENTAL PROGRESS

A. Development of Ground-Coat Enamel

The ground-coat enamels recommended for use on this project, when applied to AISI C-1012 steel, left two things to be desired. First, fish scaling was present unless extreme care was taken in cleaning the steel prior

to coating. Second, thermal-shock resistance was acceptable only occasionally and with extreme difficulty. These coatings proved successful only when applied to steel containing 0.03 per cent carbon.

Porcelain enamels which have been proven satisfactory for coating steel-plate sections subject to thermal shock have not been made available for use by this laboratory.

At this point, it became evident that a coating with better fish-scale and thermal-shock resistance must be obtained, therefore, it was decided that an effort would be made to develop such a coating.

The ground-coat enamels thus far used matured between 1560° and 1620° F. The cover-coat enamel with the desirable qualities of thermal-shock resistance and acid resistance matured at 1520° F. Thus, it was considered desirable that the ground-coat enamel should be fired somewhat above this temperature.

As a starting point, a ground-coat blend which matured at 1400° F was chosen. To this blend was added A-1 aluminum oxide in increments of 5 per cent. Each addition required a 50° F increase in maturing temperature to maintain a constant degree of adherence. With an alumina content of 20 per cent and a firing temperature of 1600° F, amazing flexibility of coating was observed when the enameled piece was impacted to determine the adherence. It was assumed that this flexibility should also aid in thermal-shock resistance.

During the development of this coating, it was necessary to obtain a new supply of A-1 alumina. This new alumina did not produce the same degree of elasticity as that originally used. Examination revealed that this difference was probably caused by a difference in particle size, the new A-1 alumina being coarser than the original. Since the original alumina was added to the slip after milling, it was found that this new alumina could be added to the

mill during milling. Under these conditions, the resulting enamel had the same properties as the enamel which contained the original alumina added after milling.

T-joint specimens were fabricated from the AISI C1012 steel used previously. Specimens were coated with one and two coats, varying in total thickness from 6 to 20 mils. These T-joints were thermal-shocked according to the schedule specified in MIL-P-16961. In no instance was there a failure noted. The only evidence that the T-joints were thermal-shocked was the appearance of very small chips on the sharp edges of the steel.

An additional T-joint specimen was fabricated and coated with 6 mils of this enamel. After it had passed the thermal-shock schedule of MIL-P-16961, it was subjected to an additional five quenches from a temperature of 1000° F. The specimen was still apparently unaffected after this additional thermal shocking.

With three ground-coat enamels of varying degrees of fish-scale and thermal-shock resistance, a much better condition existed for evaluating the enameling properties of steel plate.

B. Hydrogen Studies

Previous tests to determine the amount of hydrogen diffused through or extracted from steel indicated that only the hydrogen-extraction test provided data with sufficient reproducibility to warrant further study.

This test, as described in Summary Report No. 1, depended upon hydrogen being liberated from fish scales formed in the enameled piece. It was desirable, however, to determine the amount of hydrogen injected into a given steel whether the enamel fish-scaled or not.

Another disadvantage was apparent in the previously described test. When considerable fish scaling was produced in a specimen, it was not possible to

collect all of the hydrogen liberated. This resulted from the fact that as the specimen cooled through the range of 300° to 500° F, fish scaling commenced. In this temperature range, very little time is required for hydrogen to diffuse through and out of steel, and yet the specimen was still too hot to be set up in the apparatus. In order to overcome the slow cooling of the sample and at the same time prevent the test from being dependent upon hydrogen being liberated only through the fish scaling of the enamel, the following procedure of sample preparation was developed.

The specimen was enameled in the desired atmosphere as in the previous test. However, upon being removed from the furnace, it was immediately plunged into ice water. As soon as it was cool enough to handle, the specimen was sandblasted and set up in the extraction apparatus.

By this technique, the metal cooled rapidly through the temperature range in which hydrogen diffuses most readily through steel. By removing the coating, the hydrogen was free to leave the steel without the necessity for the coating to fish scale.

To date, it has been found that the test was sensitive to coating thickness and rate of flow of the desired atmosphere into the furnace. Therefore, these conditions will be controlled in future studies of furnace-atmosphere moisture, metal thickness, metal surface treatment and steel composition as related to the amount of extractable hydrogen injected into the steel by a given enamel.

IV. FUTURE WORK

Samples of AISI C1012 steel have been received which have been subjected to various degrees of shot peening. The variables of shot size, velocity and exposure time are represented by these specimens. These variables will be

correlated with degree of surface cold working as determined by photomicrographs, and these in turn with the amount of hydrogen extracted from the steel after enameling with a given coating.

Arrangements have been made to have cold and hot reduction of a given sample of steel to several thicknesses. Upon receipt of these samples, the effect of the type of reduction on the enameling properties of the steel will be studied.

In order to study the variable of metal thickness alone, four samples were cut from the same piece of AISI C1012 steel plate of 5/8-inch thickness. Pieces were machined to thicknesses of 1/2 inch, 3/8, 1/4 and 1/8 inch. The amount of extractable hydrogen after enameling will be determined as a function of thickness and correlated with fish-scale resistance under the same conditions of thickness.

Respectfully submitted:

J. D. Walton
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
Chemical Sciences Division

Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
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Atlanta, Georgia

SUMMARY REPORT NO. 3

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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NOVEMBER 30, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SUMMARY REPORT NO. 3

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

By

J. D. WALTON

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NOVEMBER 30, 1955

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This Report Contains 11 Pages

LIST OF FIGURES

I. SUMMARY

Hydrogen-extraction studies have been made of six grades of low-carbon steels. Variables of furnace atmosphere moisture, cold working by shot peening, metal thickness, firing time and method of cleaning were also studied in relation to the hydrogen extracted and the occurrence of fish scaling.

The equipment necessary for determining adherence of enamel to steel plate has been set up. The adherence under the variable conditions cited above will be determined and tabulated with hydrogen-extraction data.

It is anticipated that studies of surface wetting will commence during the next month.

II. INTRODUCTION

This project was initiated on January 15, 1955, and has as its objectives:

1. To determine the factors which affect the enameling characteristics of steel plates and weldments.

2. To establish the validity of parameters and to set limits for controlling the quality necessary for enamelability of steel plates and weldments.

3. To assess the factors responsible for defective coated parts intended to conform to specification MIL-P-16961.

This summary report covers the period of October 1 through November 30, 1955.

III. EXPERIMENTAL PROGRESS

The hydrogen-extraction apparatus described in Summary Report No. 1 and shown in Figure 7, page 13, was modified in the following manner. The bell-jar portion of the apparatus was constructed in two sections. The upper

section was composed of a 1-inch Pyrex glass pipe nipple with the standard taper joint welded to one end. This was permanently secured to a 2- by 1-inch reducer by means of flanges designed for that purpose. A seal between the two joints was effected by means of a Teflon gasket. The 2- by 1-inch reducer was then secured to the stainless-steel base plate and served to contain the steel specimen and mercury. A Teflon gasket likewise provided a vacuum-tight seal between the glass pipe and the stainless-steel plate. Three stainless-steel pins silver-soldered in the stainless-steel plate served to hold the specimen in a vertical position.

The following procedure was used in determining extractable hydrogen.

The enameled 2- by 1-1/2-inch specimen was quenched in ice water immediately upon removal from the furnace. As soon as the piece was as cool as the surrounding water, it was dried, sandblasted and set up in the extraction apparatus. Mercury was added to cover the specimen, and the system was evacuated in order to remove any entrapped gases. The gas burette was then placed on the standard taper joint, and the remainder of the system was filled with butyl phthalate. The apparatus was then placed on a hot plate and heated to 175° C.

All firing was done in a small muffle furnace. The moisture in the furnace atmosphere was controlled in the following manner. Compressed air was controlled by means of a reducer valve to a rate of flow of 200 cc/min as measured by means of a flow rater. The air was then bubbled through water which half filled a filter flask and then through a stainless-steel tube inserted into an observation hole in the door of the furnace. The specimen was fired by passing air into the furnace for a period of 10 minutes, after which time

the tube was removed from the furnace door, the specimen placed in the furnace and the tube reinserted into the furnace.

IV. RESULTS

The C-1012 hot-rolled steel strip 3/16 by 4 inches, obtained from Atlantic Steel Company, was used in obtaining the data shown in Figure 1 to study the effect of moisture in furnace atmosphere and firing time and all the data represented in Figures 2 and 3. The thickness curve of Figure 1 represented by A, B, C and F was obtained by machining from one 4- by 3-inch piece of 5/8-inch C-1012 steel flat four 1-1/2- by 2-inch specimens to the thicknesses shown. Point F represents the 5/8-inch-thick specimen without machining. The curve represented by D, E and F was obtained by securing C-1012 strip in the desired thickness.

Figure 2 represents the data obtained from samples of 3/16-inch C-1012 steel receiving various degrees of shot peening. The curve representing shot size was obtained from samples subjected to a constant shot exposure time of 15 minutes and constant shot velocity resulting from a wheel speed of 2250 rpm with the shot size which varied from S-70-WSS to S-230-WSS. The shot-velocity curve was obtained from samples receiving the same exposure time as the previous test and the shot size held constant at S-170-WSS but with the velocity of the shot resulting from a wheel-speed variation from 1500 to 2470 rpm. The exposure-time curve represents the variable of time from 5 to 30 minutes with a wheel velocity of 2250 rpm and shot size of S-170-WSS held constant.

Samples of 4- by 4- by 3/16-inch C-1012 steel strip were cleaned by sodium hydride pickling. The hydrogen extracted after coating the sandblasted and unsandblasted sections is shown in Figure 3.

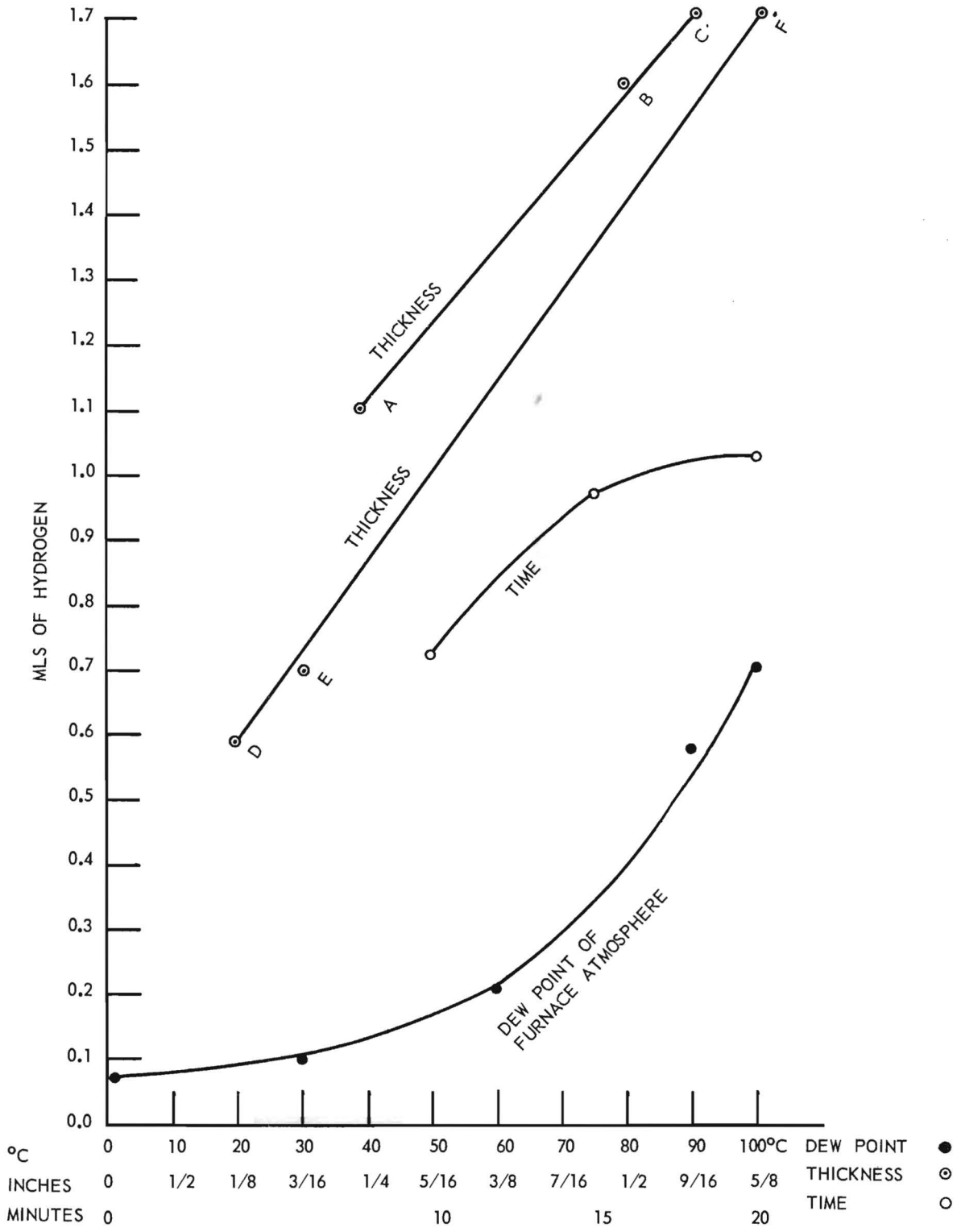

Figure 1. Effect of Metal Thickness, Firing Time and Amount of Moisture in Furnace Atmosphere on Amount of Hydrogen Extracted.

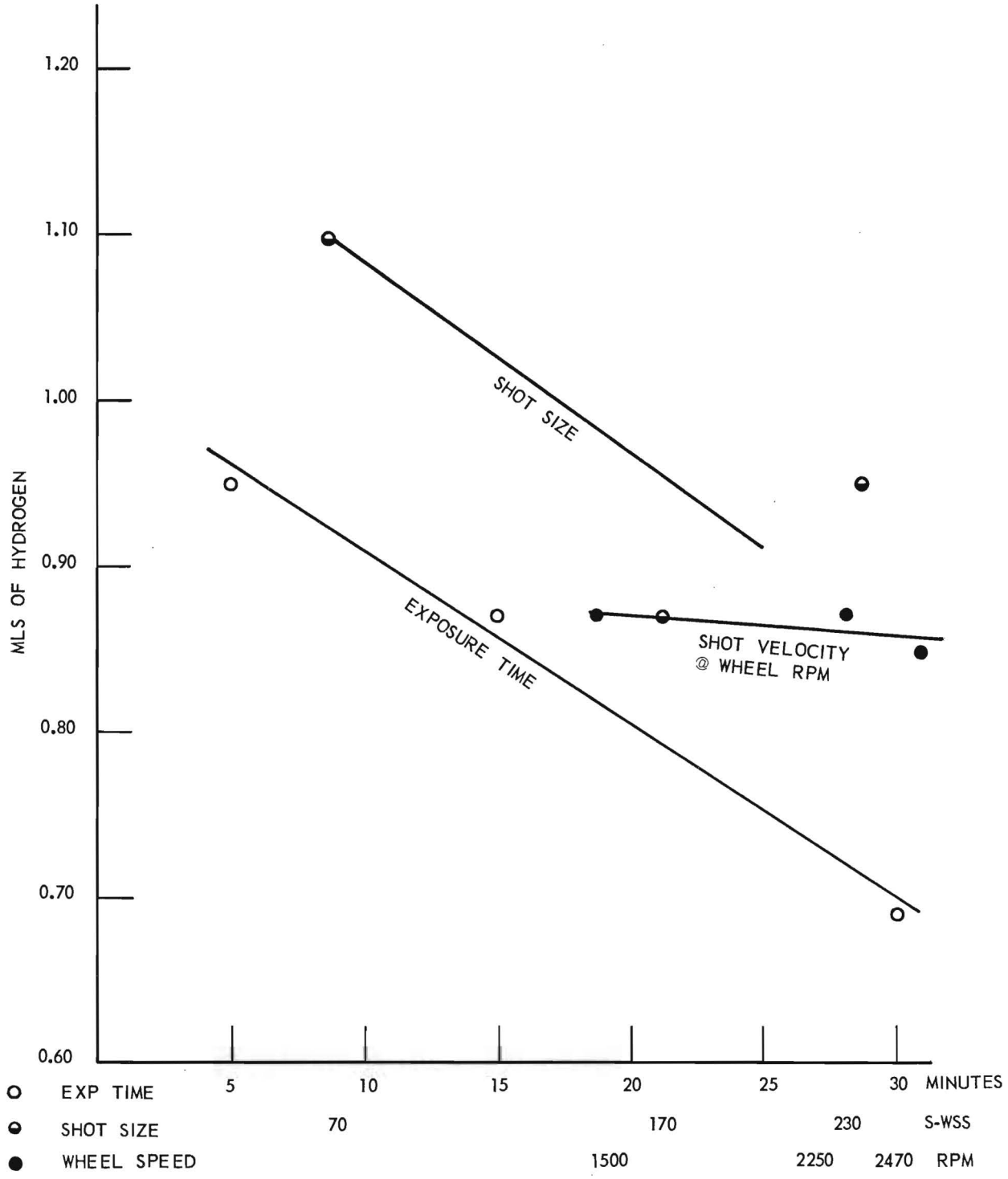

Figure 2. Effect of Shot Peening on the Amount of Hydrogen Extracted.

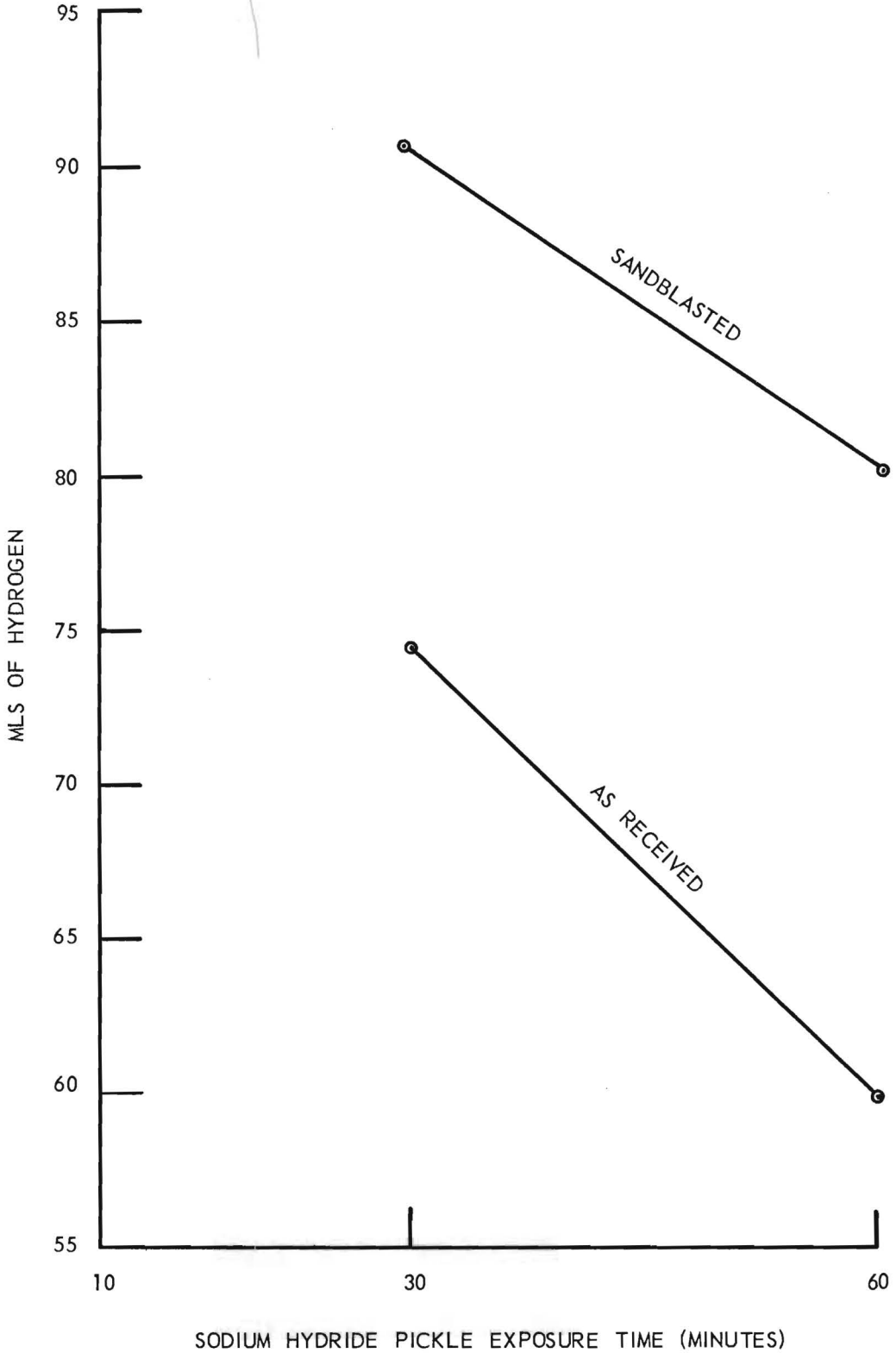

Figure 3. Effect of Sodium Hydride Pickle Time on Amount of Hydrogen Extracted.

All of the data reported were obtained from samples fired in a furnace atmosphere provided by air passing through boiling water and entering the furnace as previously described with the exception of the data from which the curve representing dew point of furnace atmosphere in Figure 1 was obtained.

Table I lists the analyses of the steel samples used in this study.

V. DISCUSSION OF RESULTS

A. Hydrogen-Extraction Data

From Figure 1, it can be seen that thickness, amount of moisture in the furnace atmosphere and firing time were important in determining the amount of hydrogen injected into steel.

The curves representing hydrogen extracted as a function of steel thickness suggest two things. First, the amount of hydrogen is a linear function of thickness, and, second, the surface of the steel itself is an important factor in the injection of hydrogen into the steel. The specimens representing points A, B and C were obtained by reducing the thickness of specimen F through machining off the surface. Specimens D, E and F were received as hot-rolled strips. The displacement of curve A-C from D-F would, therefore, appear to be due to the difference in the surface the specimens used. All specimens were sandblasted prior to enameling.

The variable of time appears to be important only to a point. If we assume that most of hydrogen injected into the steel results from the reaction between the glass and the steel, then the greatest change in the rate of reaction would occur in the early stages of firing. This is indicated by the time curve of Figure 1.

TABLE I

Type of Steel	Form	Thick-ness (in.)	Analysis C	Mn	P	S	Cu	Si	Cr	Ni	V	Mo	B	Gas (ml)	Fish Scale
C1006	1-1/2-inch strip	1/8	.08	.34	.010	.036	.34	----	---	---	---	---	-----	0.67	Slight
C1012	1-1/2-inch strip	1/8	.12	.44	.010	.034	.37	----	---	---	---	---	-----	0.59	Slight
C1017	1-1/2-inch strip	1/8	.16	.43	.010	.028	.32	----	---	---	---	---	----	0.71	Slight
C1012	4-inch strip	3/16	.12	.48	.010	.010	.23	----	---	---	---	---	-----	0.70	Severe
Capped	Plate	3/16	.06	.36	.010	.026	---	.008	---	---	---	---	-----	0.79	Slight
Rimmed	H. R. Coil	0.17	.07	.38	.006	.025	.02	.007	.01	.02	---	---	-----	0.52	Very Slight
Rimmed	C. R. Coil	0.126	.07	.38	.006	.025	.02	.007	.01	.02	---	---	-----	0.74	None
Lukens T-1	Plate	1/4†	.15	.75	.026	.026	.36	.24	.50	.85	.05	.45	.0029	1.11	None

†Typical analysis

NOTE: All samples were sandblasted prior to enameling.

The curve representing the effect of moisture content of the furnace atmosphere was as expected. The temperature scale represented the temperature of the water through which the air entering the furnace was passed.

In Figure 2, it was noted that exposure time had the greatest effect on hydrogen diffusion and shot velocity the least effect. Shot size did not produce too well-defined data. It is possible that a maximum degree of resistance to hydrogen diffusion was obtained at a shot size of S-170-WSS. However, with no further data to substantiate this possibility, a straight-line curve was used to depict the effect of this variable.

The effect of sodium hydride pickling on the amount of hydrogen extracted, with and without sandblasting is shown in Figure 3. Both curves indicate that the time immersed in the sodium hydride pickle decreased the amount of hydrogen extracted from the steel. The sandblasting, however, increased the amount of extracted hydrogen. This should not be taken necessarily as a detrimental effect. It is very probable rather that this indicated a greater degree of reactivity between the steel and the glass.

Referring to Table I, it can be seen that no evident correlation exists between fish scaling and amount of hydrogen extracted. In the case of the hot-and cold-rolled rimmed steel, the amount of hydrogen extracted as related to thickness was reversed from that obtained when thickness alone was studied in Figure 1. Thus, it would appear that method of reduction was a more important factor than the thickness alone.

B. Fish Scale

In all cases where possible, 4- by 4-inch plates of each of the steels on which hydrogen-extraction data were obtained were coated under the same conditions, and the degree of fish scaling was observed.

With the exception of curve A-C and D-F, all the steel specimens used to obtain the data for Figure 1 were prepared as described previously. The range of firing time investigated had little effect on the fish scaling of the samples. All specimens exhibited this defect to a considerable degree. In the case of varying the saturation temperature of air entering the furnace, fish scaling did not appear until the temperature of the water reached 30° C, and then only two fish scales appeared on a 4- by 4-inch plate. The fish scaling increased in severity as the saturation temperature increased beyond 30° C.

All of the shot-peened samples exhibited severe fish scaling. However, many of the fish scale exposed clean metal below. This would appear to indicate that poor adherence was developed between the glass and the steel. This was further evidenced when the 1-1/2- by 2-inch specimen was quenched after enameling, causing a large portion of the coating to spall from the section. Thus, although the extractable hydrogen varied somewhat because of shot peening, the degree of adherence appeared to be below a level at which the coating could resist fish scaling.

This was further evidenced in the case of the sodium hydride pickled specimens. The samples coated "as received" spalled badly upon quenching. However, the hydride pickle followed by sandblasting provided a surface to which the glass adhered very well and did not spall when quenched. Likewise, after sandblasting, the extractable hydrogen increased almost 30 per cent over that obtained when the specimen was not sandblasted prior to enameling. In this instance all plates, sandblasted or not, exhibited slight fish scaling. It might appear possible that, in this case, the improved adherence merely increased at a rate comparable to the increased hydrogen produced, with the net resistance to fish scaling remaining constant.

VI. FUTURE WORK

Micrographs are being prepared of all specimens in order to evaluate better the interface condition as related to adherence, fish scale and extracted hydrogen.

Since it has become evident that more statistical information is needed as to the actual adherence developed between the glass and the steel, the necessary arrangements have been made for stretching the steel strips to a predetermined percentage of elongation and determining the adherence by means of a P.E.I. adherence meter. Concurrently with this program, a study of the wetting characteristics of the various steels will get under way.

Respectfully submitted:

J. D. Walton
Project Director

Approved:

Wyatt C. Whitley, Acting Chief
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Paul K. Calaway, Director
Engineering Experiment Station

ENGINEERING EXPERIMENT STATION
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SPECIAL REPORT NO. 1

PROJECT NO. A-204

PORCELAIN ENAMEL DEFECTS
LITERATURE REVIEW AND DEFINITIONS

By

CHARLES E. COLLUM, GILBERT STEINER,
and T. ALLEN WASTLER

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SEPTEMBER 1, 1955

ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

SPECIAL REPORT NO. 1

PROJECT NO. A-204

PORCELAIN ENAMEL DEFECTS
LITERATURE REVIEW AND DEFINITIONS

By

CHARLES E. COLLUM, GILBERT STEINER,
and T. ALLEN WASTLER

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SEPTEMBER 1, 1955

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I. INTRODUCTION

This literature review was undertaken as part of an U. S. Department of the Navy contract entitled "Porcelain Enameling Quality Steel Plates and Weldments" which was initiated at Georgia Institute of Technology on January 15, 1955.

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II. PURPOSE

It is the purpose of this report to describe the defects in enamel coatings on steel plate as discussed in the literature and to report the suggested causes and prevention of defects. Because of the scarcity of references pertaining to steel plate and because the authors feel that many of the defect-producing mechanisms are independent of metal thickness, phenomena associated with defects on sheet steel and stock of other metals have been reviewed. A large portion of the material included refers to the difficulties encountered in enameling sheet stock (stock less than 3/16 inch thick).

Over 100 separate names for enamel defects have been noted in this literature survey. In many instances, lack of standardization has apparently resulted in an overlapping or duplication of terminology. In cases where there seems to be duplication, the authors have attempted to standardize the nomenclature by cross-indexing alternative names to the most descriptive and most popularly used terms.

It is most difficult to predict and to cope with defects of a delayed nature, such as fish scaling. For this reason, emphasis has been placed on a review of the literature regarding fish scales.

References pertaining to enamel defects were located by using the following bibliographic journals.

1. Enamel Bibliography and Abstracts, 1928 to 1939 inclusive; compiled by E. H. McClelland, Edited and Published by the American Ceramic Society, Inc., 1944.
2. Enamel Bibliography and Abstracts, 1940 to 1949 inclusive; compiled by Roger L. Fellows, Edited and Published by the American Ceramic Society, Inc., 1953.

3. Ceramic Abstracts, 1949 through March 1955.

4. Chemical Abstracts, 1949 through March 1955.

5. A.S.M. Review of Metal Literature, 1949 through 1953.

6. Bibliography of Non-Metallic Inclusions in Iron and Steel, Pittsburgh Carnegie Library, Technology Department.

7. Engineering Index, 1949 through 1954.

8. Chemisches Zentralblatt, 1949 through 1954.

The two issues of Enamel Bibliography and Abstracts were considered to contain essentially complete reference to material regarding enamel defects or defect-producing mechanisms published from 1928 to 1949 inclusive. The abstracts in these two journals were completely reviewed. The literature survey was completed through March of 1955 primarily by using Ceramic Abstracts. Particular emphasis was placed on the section of this journal entitled "Enamels and Refractory Coatings for Metals." The other abstract journals were reviewed by checking the sections concerning enamels and related topics.

A number of miscellaneous bibliographies were found to be of value in completing this survey. The works of Zapffe and Sims (378), B. J. Sweo (336), and Hoff and Klårding (161) contained extensive bibliographies, and the work compiled by Zapffe and Sims covered the period from 1898 to 1939.

Over 300 references pertaining to enamel defects in general were reviewed for this report. Some of the articles reviewed contained information of dubious value and, therefore, have not been included in this report. All others have been cited even though some of these contain only general observations or opinions. Approximately 100 additional references considered potentially worthwhile but not reviewed have also been included. About 25 per cent of the total

number of references were in foreign-language periodicals. One-quarter of these, representing work of the most important writers, were reviewed and have been cited.

III. SOURCES OF ENAMEL DEFECTS

Enamel defects result from the effects of many factors. Generally spea no one factor is entirely responsible for the occurrence of any defect. On contrary, it may be necessary for a number of conditions to exist simultaneo before a particular defect will occur. A complete understanding of a defect may develop only after an investigation and analysis of the base metal and i properties, the characteristics of the bisque or fired coat, and any one or several of the steps of metal and enamel processing.

In this report, the factors which have been described in the literature responsible for enamel defects are classified according to their relation to materials used and the processes involved. The reader should recognize that many of these factors are interrelated.

Materials as Sources of Enamel Defects

The Enamel as a Source of Defects

Such factors as composition and set of the slip, strength, structu and thickness of both bisque and fired coat, fluidity and surface tension of molten enamel, and coefficient of thermal expansion of the fired coating are variables which must be considered as sources of defects.

The properties of an enamel depend, to a large extent, upon the materi used in its preparation. It is well recognized that variations in the form lation of a given enamel may impair or enhance its resistance to the various fects. As a result, components of an enamel may be either directly or indi responsible for defects, imparting desirable characteristics to one enamel contributing directly to the formation of defects in other enamels.

Components which liberate gaseous materials at elevated temperatures during enameling may contribute to defects in any enamel, and this hazard should be carefully considered.

Set. The set or consistency of a milled enamel slip is important in producing good quality enamel surface. Spraying of low-set and low-gravity slip (high water content) may result in an orange peel or blown finish (68). Pieces dipped or drained in a low-gravity slip frequently exhibit run-down or sagging in the wet enamel on vertical surfaces (218). Dusting is likely to occur in spraying a high-set slip (68).

The set of the enamel slip may be adjusted by the addition of various materials to prevent defects of this kind. Electrolytes or set-up salts such as borax, magnesium carbonate, sodium aluminate, and barium carbonate are frequently added to increase the set (68). Other electrolytes such as tetrasodium pyrophosphate are used to reduce the set of an enamel.

Coating Strength. The strength of both bisque and fired coat must be sufficient to reduce defects to a minimum. The strength of the bisque and the fired coating may be improved by certain additions to the enamel. The film strength of the dried enamel bisque must be great enough to prevent defects such as curling, pop-off, and tearing. Film strength has been improved in some enamels by the addition of gums and alginates to the mill (68). Excessive amounts of the material should be avoided since a poor surface of fired enamel will result. Resistance to mechanical and thermal shock may be increased by adding sodium oxide to the enamel (148). High feldspar content, on the other hand, tends to decrease the shock resistance of the fired coating.

Strength of the fired coating is also a function of the firing temperature and firing time (378, 381). Underfiring generally produces a weak coating, which may fail if subjected to the strains or forces of fracture-type defect mechanisms. Overfiring tends to produce a glassy, brittle coating, which also has lowered resistance to fracture-type defects.

Enamel Structure. Poor enamel structure may lead to defects. As has been previously mentioned, glassy enamels frequently have a tendency to fail. Enamels with well-developed bubble structures generally have a superior resistance to defects (381, 216). Coatings with a large number of relatively small bubbles, especially bubbles close to the metal-enamel interface, are particularly resistant to fish-scale-type defects (270, 59). It is presumed that these bubble dissipate the pressure of gases at the metal-enamel interface. The bubble structure of enamel is also a favorable factor in preventing defects such as hairlines (102). However, bubbles in the enamel can become excessive and produce a spongy texture (311, 416), or they can be too close to the surface and produce blister- or crater-type defects.

Gases liberated during firing or gases present in the furnace atmosphere are responsible for the bubbles in the fired enamel. Clays impart the bubble structure to a fired enamel (159, 270). Opaque clays generally impart a desirable bubble structure. Clear-firing clays, on the other hand, tend to produce an enamel with poor bubble structure (159, 199, 216, 182, 217). Poor bubble structure may also result from the fluxing action of certain materials. Iron oxides produced during enamel firing may fine out the structure and increase the tendency of the enamel to be defective (159).

Coating Thickness. The thickness of the bisque and fired coating may contribute to or limit the formation of defects. The bisque must be applied sufficiently thick to avoid bare spots and burn-off. However, this coat must not be so thick that cracking, crawling, curling, and tearing will occur. Thick coats tend to limit the evolution of gases responsible for defect formation. However, thin coats are susceptible to defects caused by bubbles at the surface which may expose the base metal to the oxidizing atmosphere of the furnace (74).

Fluidity and Surface Tension. The fluidity and the surface tension of the molten enamel must be such that smooth uniform films are obtained in firing. These properties must also be such that discontinuities in the molten coating such as broken blisters and hairlines are healed during the firing operation. The fluidity of the molten enamel is an important factor in its ability to free itself of gases and, thus, prevent or control reboiling and blistering. Addition of materials such as titanium oxide (193) and lithium silicate (125) frequently increases the fluidity to the desired degree. In some instances, differences in fluidity will result at various points on the surface. Impurities at isolated points may act as a flux and increase the fluidity of the contaminated area to such an extent that depressions or pits can occur (288, 369).

Thermal Expansivity. The thermal coefficient of expansion of a fired enamel coating must be such that the enamel "fits" the base metal. The most desirable fit of an enamel to a metal is one of compression in the enamel layer (68), not a condition of freedom from stress. The expansion of enamel with increasing temperature or contraction with reduction in temperature may be sufficiently different from that of metal in a system of improper fit that the

resultant strains produce a defective coating. Strains of this nature reporte cause crazing (218), hairlining (114), and thermal-shock failure (21). The enamel composition can be controlled to produce a proper fit.

Gas Evolution. Gases evolved from the enamel during firing are particularly important sources of enamel defects. Gases are directly responsi for both blister- and fracture-type defects in enamel coatings (378). Blister ing, boiling, etc. occur in the molten enamel as a result of gases evolved during firing. Fish scales, chips, fractures, etc. occur in the hardened coat ing as a result of the pressure of the gas retained by the piece.

The gases associated with enamel are water, carbon dioxide, fluorine, chlorine, oxides of nitrogen, ammonia, and sulfur-bearing gases (336). Water driven from the enamel is significant in the formation of enamel defects in that it reacts with the ferrous enameling metals at firing temperatures to pro duce hydrogen. Hydrogen, unlike the other gases, readily enters the base meta and may later effuse from the metal to give rise to either blister- or fractur type defects. Water responsible for hydrogen formation includes the milling a quenching water, the chemically combined water in the clay and the dissolved water in the frit (270).

Carbon gases may result from decomposition of organic material contained i the clay or from decomposition of carbonates in the enamel or in the milling water. These gases give rise to blistering and boiling of the enamel coating (368, 379). Chlorides and fluorides as mill additions also cause blistering (336). Sulfate set-up salts, such as magnesium sulfate, are known to liberat sulfur gases at elevated temperatures and produce scumming, shorelining, pitt and devitrifications (68).

The Base Metal as a Source of Defects

The selection of a base metal for an enameled product should be based not only on its fabricating qualities and dimensional and strength requirements but also on its ability to enamel without defects. Characteristics of a base metal which may affect the enameling quality of the metal are the composition, the structure, the nature of inclusions, the resistance to deformation during enameling, and the thickness.

Composition and Structure. The steel used as a base in enameling is a metal of relatively low carbon content. The carbon content of mild steel is approximately 0.06 to 0.08 per cent while that of enameling iron is only 0.03 per cent. Small amounts of manganese, silicon, and phosphorus are found in both types of metals. Additional elements, such as titanium and chromium, are added in the production of special enameling steels.

Steels are mosaic structures composed of metallic and nonmetallic crystals and grains. The grain structure may be well-ordered and homogeneous in some metals and deformed and discontinuous in others. The grains themselves are subdivided by slip and cleavage planes, which provide a network of ultramicroscopic discontinuities. Gases may collect in such discontinuities and thus be available to produce blistering during firing and fish scaling after firing (378).

Rimmed steel, which is frequently used in enameling, is interesting in that it contains both homogeneous and heterogeneous metal. The rimmed ingot is one with a homogeneous rim and a core containing impurities and blowholes. When the rimmed ingot is rolled, the heterogeneous core remains sandwiched between two layers of rim metal. The core metal extends almost to the edge of the rolled metal on all four sides.

Working of steel affects the grain structure of the metal. Cold working, for instance, opens the grain structure. This is substantiated by density measurements, which indicate an increase in the specific volume of cold-worked metal (378). Rolling and blasting deform the grains, especially those on the surface, and rolling imparts a laminar structure to the steel in the rolling direction. Both actions control gas effusion from the metal and tend to elimi- nate the occurrence of enamel defects.

Inclusions. Inclusions, impurities, and gases found in steel accoun for many of the defects occurring in enamel coatings on such metals (378, 381, 159, 105, 336). These foreign materials may be found in microscopic interstic or in macroscopic voids in the metal structure, or they may be found in solu- tion. Of the foreign materials considered, hydrogen gas is by far the most important source of defects. Many of the defect mechanisms associated with enameling certain metals are explained by hydrogen action. For this reason, an understanding of the behavior of hydrogen in enameling metals is necessary if the cause of certain defects is to be explained.

Hydrogen in the dissociated or atomic state will enter into and diffuse throughout the ferrous metals normally used in enameling. Molecular hydrogen, on the other hand, is considered to be practically nondiffusible. Several writers (378, 336) report that hydrogen in the molecular form dissociates to atomic hydrogen in the presence of the metal at approximately 800° C and, in this state, readily enters the metal. Atomic hydrogen provided with a driving force diffuses into or effuses from homogeneous metal, such as the rim portion of rimmed steel, at any temperature. However, below 800° C if diffusing hydrc encounters voids or discontinuities such as those found in the core portion of

rimmed steel or in cold-worked metal, association to molecular hydrogen occurs, and the nondiffusible molecules become trapped and retained in the voids. Upon heating above the dissociation temperature of the trapped hydrogen, for example in firing enamel, the gas becomes diffusible and may again spread throughout the metal surrounding the discontinuity. With properly directed driving force, the hydrogen may escape from the metal.

The solubility of hydrogen in steel increases as the temperature is raised (under a given pressure of hydrogen) until at enamel-firing temperatures the solubility is approximately 1000 times that at room temperature (378). Of course, the solubility will tend to be low even at enamel-firing temperatures if the external pressure of hydrogen is small. The increase in hydrogen solution greatly exceeds hydrogen evolution which makes possible the retention of relatively large amounts of hydrogen within the metal structure. On cooling, molecular hydrogen which dissociated and dissolved at high temperatures precipitates from the metal lattice as atomic hydrogen. Diffusion of the precipitating gas continues at room temperature until equilibrium is established. The diffusing gas at this temperature is either occluded as molecular hydrogen in discontinuities or reaches the surface of the metal and escapes.

Both molten and hardened enamels impede the progress of effusing hydrogen. Hydrogen expelled from beneath an enamel-coated metal at high temperatures is responsible in full or in part for producing bubbling, boiling, reboiling, and blistering in the molten enamel (378, 381, 336, 380, 375). The gas diffusing at room temperature encounters the relatively impermeable hardened enamel coating and collects under such a pressure at the enamel-metal interface that chips, fish scales, shiners, and other delayed defects may be formed (381, 375).

The physical changes produced in the base metal during the working operations appear to influence the behavior of hydrogen. The open structure produc in cold working accelerates either absorption or effusion of hydrogen, dependi upon the nature and direction of the driving force. Generally speaking, more dissolved hydrogen is evolved at elevated temperatures from cold-worked metal than from other types (159). Blisters will appear preferentially over a scratched section of a metal surface during firing. The scratch, essentially cold-worked area, appears to absorb greater quantities of hydrogen than the su rounding metaland will, consequently, evolve greater amounts of gas when heated an elevated temperature (378, 374). Also the open structure makes possible ar increase in the volume of trapped gas. The increased trapping action of cold-worked metal, together with increased volume of voids, reduces the effusion of hydrogen from the metal at room temperature. The fact that quantities of hydr gen may be expelled from cold-worked metal on heating and that the voids trap hydrogen, which reduces the effusion at normal temperatures, accounts for a reduction in the tendency of enamel on these metals to exhibit gas-caused delayed defects.

The banded structure in steel developed in rolling tends to prevent the effusion of the gas in a direction normal to the plane surface. Hydrogen, th fore, diffuses preferentially within the rolling plane of the metal (378). This is borne out by the frequent observation of gas-caused defects that occu only on the edges of an enameled piece.

Hydrogen in steel is derived from the raw materials which enter into th metal making from moisture in both metal-making and enameling furnaces, from pickling and cathodic electrolysis, from neutralizing, from rusting, and fro

water driven from the enamel during firing (378, 336, 159, 380). The total quantities of hydrogen available and retained during each of the operations must be considered in defect formation. The hydrogen derived from any source may become important for a given enameling operation.

However, an analysis by Moore et al. (270) indicates that water driven from the enamel, particularly the water dissolved in the frit, accounts for the major part of the hydrogen retained by the metal. It was pointed out by Sweo (336) that one significant source not included in the analysis made by Moore was the effect of moisture in the furnace atmosphere during firing. He intimated that since only approximately 50 per cent of the total hydrogen was accounted for by the sources included, moisture in the furnace might be a particularly important source of hydrogen.

Walton* found that when water is sprayed over enameling metal at firing temperatures, only a nominal amount of hydrogen was retained by the metal. He also found that the amount of hydrogen introduced by this means was not so great as that introduced into the metal when it is coated and fired in a moist atmosphere. This would indicate that nascent hydrogen is introduced into enameling metal not only as a result of the iron-water reaction at the interface but possibly by an additional mechanism.

The theory proposed by Dietzel (111), Moore, et al. (273) for adherence may explain this additional mechanism. The molten ground coat enamel is an electrolyte at the firing temperatures from which cobalt plates out. Once the cobalt contacts the iron, tiny galvanic cells are established. The galvanic

* Walton, J. D., Interim Report No. 1, Contract No. NObs 66521, Bureau of Ships, Department of the Navy.

action produces a reducing condition capable of dissociating water to form nasc hydrogen. Such hydrogen could enter the base metal.

Moisture in the furnace atmosphere appears to control the amount of water in the enamel during firing. If the firing atmosphere is excessively moist, th supply of water in the enamel is maintained at a level capable of producing lar quantities of defect-producing hydrogen. On the other hand, if the humidity is low, water tends to leave the enamel with a resulting decrease in hydrogen for- mation. Gas-caused defects are, therefore, less likely to occur if the furnace humidity is maintained at a low level.

Other gases associated with the base metal which are regarded as adversely affecting an enamel coating are: carbon dioxide, carbon monoxide, methane, nitrogen, and water (336). These gases, all relatively insoluble in steel, are generally considered to contribute only to a small extent to the formation of enamel defects. The carbon gases--carbon monoxide and carbon dioxide--produced by direct oxidation of carbon in the metal during enamel firing may be partly responsible for boiling-type defects appearing at high temperatures (378). Any of these gases present at the interface of the metal and hardened enamel may contribute to the total gas pressure required to produce delayed defects.

Solid inclusions are also related to defect formation. Zapffe (378) intro duced various materials as artificial inclusions in steel and observed defects in the enamel coat directly over the inclusions. The inclusion is a hetero- geneity in and around which diffusing hydrogen becomes trapped and stored and available for producing blistering and reboiling at high temperatures and de- layed defects at room temperature. The inclusion or impurity may also be mate which reacts chemically with elements available during enamel firing to produc

more or less stable compounds, which are either retained by the metal or liberated as gaseous materials. The compounds retained by the metal may dissociate in firing at higher temperatures to produce gases contributing to gas-caused defects. Gases, such as the carbon gases mentioned previously and methane formed by hydrogen action, are so produced (378, 377).

Resistance to Deformation. The sag and warp resistance of the base metal must be sufficient to hold the shape of the piece during firing. Failure of the metal to have suitable resistance results in enamel failures such as sagging and crazing (68).

Sag and warp resistance are functions of both metal composition and gauge. Mild steel shows comparatively low resistance to sagging and warping. Enameling iron with lower carbon and manganese content shows a resistance superior to that of mild steel. Special steels such as titanium-bearing steels also have comparatively high strength at enameling temperatures, with resultant good sagging and warping resistance.

Thickness. Defect formation is found to be a function of the thickness of the base metal. An enameled wedge of mild steel which had been aged at elevated temperature was found to have a satisfactory coating over the thin tip section but a defective coating over the thicker portion (378). The distribution of defects may be attributed to the behavior of hydrogen by two different actions. Hydrogen diffusion through steel increases with decreasing thickness of metal and with increasing temperature (limited by solubility). In the aging operation, hydrogen had sufficient time to be expelled from the tip but evidently not sufficient time to be completely evolved from the thicker sections. Therefore, during firing, the remaining hydrogen was evolved in comparatively great quantities from the thicker sections and caused a greater number of defects in that area.

The difference in quality may also be explained by the fact that during firing the thin tip, unlike the thicker section, may have reached more quickly a temperature at which more hydrogen was dissolved than was evolved. If this were true, hydrogen would be so rapidly dissolved in the metal of the tip that blister-type defects could not be formed over the tip.

In general, enameled, thin sheet steel exhibits little gas-caused defects. As the thickness of the sheet increases, the amount of hydrogen retained both in solution and occluded in discontinuities is likely to be greater with a resulting increase in either blister-type defects in firing or delayed defects in hardened enamel. In some cases, however, thick metal may actually tend to allow hydrogen to become so dispersed throughout the metal that the driving force of the hydrogen is not sufficient to cause defects.

In enameling thin sheets, there is danger of sagging or crazing, as mentio in "Resistance to Deformation." However, these difficulties are not of general concern in enameling thick steel pieces.

Processing as Sources of Defects

Slip Preparation as a Source of Defects

Mixing, Smelting, and Quenching. These processes are seldom responsib for the formation of defects in the fired enamel if properly carried out. However, it is possible for impurities and foreign material to be added to the enamel inadvertently. This may come as dirt from tools or agitators (53, 227), from the furnace atmosphere (15), or from dirty water (60). Such impurities account for defects such as black specks, pits, and scale.

Milling. The milling operation is a source of several troublesome defects, many of which can be traced to over- and under-grinding. Both over- and

under-ground enamels are reported to result in bisque coat failures such as tearing and fired coat failures such as chipping, copperheading, pimples, and crawling (225, 74, 190, 330, 138, 55, 306).

The ground enamel must be mixed with the proper amount of water in order to obtain a desirable set. As has been mentioned previously, proper set must be maintained in order to prevent spraying- and sagging-type defects. The water used in milling must be sufficiently clean and free from dissolved material to reduce the tendency of an enamel to be defective. Scumming may result from the use of hard water in the mill (230, 369).

Other miscellaneous factors may result in defects. Pitting may be the result of excessive soluble salts being leached from the frit during milling (105). Lumps may be caused by poor screening (227, 53, 60). Black specks may result from foreign particles introduced in the mill (227). Iron particles not removed by the magnetic separator cause this type of defect (190).

Aging. Aging tends to increase the soluble salts in the mill liquor. As aging is increased, more salts are dissolved and the tendency of the enamel to scum decreases. On the other hand, the tendency to tear and to form pimples, copperheads, and pinholes is increased (330, 369, 57, 55).

Metal Conditioning as a Source of Defects

Forming. Defects in enamel coatings may occur as a result of the metal-forming operations. Such processes as stamping or drawing produce strains in the metal structure, which may cause hairlining and tearing in an enamel coating (303, 227).

Defects that are derived from forming operations (exclusive of rolling) are primarily the result of improper design of the piece to be enameled.

Curved surfaces of small radii, sheared edges, and nonuniform cross sections may lead to defect formation. Strains may be present in enamel coatings on curved surfaces of small radii, which frequently cause tearing and chipping (68 Blistering and flaking of enamel (378) may occur at sheared edges of plate and sheet pieces due to preferential effusion of hydrogen. Pieces of nonuniform cross section may heat unevenly resulting in stress-caused defects such as tearing, hairlining, and spalling. Hydrogen-caused defects may also appear over particular sections of nonuniform pieces.

The drawing compounds used in many of the forming operations, if not completely removed in subsequent cleaning and pickling operations, may cause defec in an enamel coating. Many of the organic-type oils on the enameling metal may react with the iron in storage to produce films of insoluble iron salts (68). Hydrous salts which decompose during enamel firing may be responsible for producing defect-forming hydrogen (336, 367).

Welding. The welding process is well-known as a source of enamel defects. The extra stress induced by heating and cooling the metal, the presenc of gases during welding, the addition of a weld metal of composition different from that of the base metal, and the various imperfections found in weldments are all found to lead to defective enamel coatings. Several defects which occur as a direct result of welding are hairlining, chipping, blistering and boiling, fish scaling, and copperheading (77).

The localized heating to which the metal is subjected during welding may produce strains causing hairlining and chipping. Hairlining may also result from a thin weld or thin spots in a weld, unwelded overlaps, spot welds spaced too far apart, and warping as a result of faulty design (77, 168). These

defects may also occur as a result of crevices left in the weld, which will open and close as the piece is worked (77, 224, 168).

Hydrogen gas is generally considered to be the most important source of gas-caused enamel defects over weldments. The gas is available in almost every type of welding and is highly soluble in both the base and weld metals at the temperatures required for welding. Cellulose-coated welding rods used in arc welding and the flame in acetylene and atomic hydrogen welding are all obvious sources of hydrogen (378). In addition, Zapffe and Sims (377) show that the moisture contained in both welding atmosphere and materials is one of the most important sources of hydrogen.

Hydrogen may be retained and trapped both in solution and in numerous discontinuities in the weld. The silvery interior and the decarburization often associated with blowholes and fissures (377) attests to the presence of the reducing gas. The presence of nonmetallic impurities, such as phosphorus, carbon, and sulfur, provides additional retention of hydrogen due to the chemically reactive nature of the materials.

The concentration of hydrogen retained in the weld and adjacent metal as a result of welding is greater than that in other sections of the piece. Hydrogen, effusing in relatively greater amounts from these localized areas than from other areas of the piece, is responsible for preferential blistering and fracturing of enamel coatings over the weld (378).

Relief from hydrogen in weld metal with a resulting elimination of defects in enamels over welds is accomplished by several operations. Cold-working metal, as described in "Forming," opens the metal structure which allows for maximum removal of hydrogen prior to enameling. Zapffe (377) reports that peening of

welds at elevated temperatures reduces the amount of hydrogen in the weld metal. He also describes the removal of hydrogen by controlled aging and annealing.

Oxides formed in welding may lead to defects such as copperhead. Imbedded scale, dirty surface, as well as irregular or overoxidation, may also cause this defect (77). Uncleaned and rough welds may lead to numerous other defects (168, 77).

Mechanical Cleaning. Sandblasting or gritblasting of the metal may cause several types of defects. There are two common defects, in particular, which can occur as a direct result of blasting.

Copperheading can occur when the abrasive is too coarse. Pits and peaks large enough to prevent a smooth enamel coating can be formed (60).

Surfaces improperly cleaned in blasting may lead to defects such as blistering (60) and jumpers and pop-offs (226).

The open structure imparted to the metal by blasting may cause an acceleration of hydrogen diffusion into or effusion from the metal. This action, described in "Forming," may result in blistering, reboiling, or fish scaling.

Chemical Cleaning. The chemical cleaning operations: degreasing, pickling, rinsing, and neutralizing are all found to be the cause of enamel defects. Chemical pickling and cathodic electrolysis, in particular, are reported as sources of defects.

In general, there are three conditions resulting from the pickling operation which could cause enamel failures. These are underpickling, overpickling, and incomplete removal of the pickling liquor from the metal surface.

Underpickling may fail to remove all scale or foreign materials from the metal surface. Black specking may result from such a condition (227).

Underpickling may also produce an insufficiently etched metal surface. Adherence failure and fish scaling (180, 229) may occur under this circumstance.

Overpickling may produce an extremely rough and overetched metal surface. This leads to a variation in ground coat pickup, which tends to produce fish scaling and chipping (229, 45, 60, 266, 129). Excessive pickling for too long a time or at too high a temperature may result in excessive gas absorption by the base metal, especially absorption of hydrogen. Hydrogen is present in the nascent form during the pickling operation and readily enters the metal. Effusion of hydrogen causes blistering, boiling, and fish scaling as well as other defects (378, 91, 324, 11). Other gases associated with pickling which may lead to defects such as jumpers, leather finish, tearing, scumming, shorelining, and pitting are sulfur gases, water, carbon oxides, and chlorine gases (336).

Inadequate cleaning of the base metal and incomplete removal of cleaning materials from the metal cause many enamel defects. Boiling or blistering may result from incomplete cleaning, rinsing, and neutralizing (91, 324, 86). Black specks and copperheading may be caused by iron-salt deposits from the pickling and neutralizing operations (227, 290, 60, 151, 57, 321). A high-salt concentration in the pickle may also lead to poor draining properties and resulting defects (228).

Nickel Flashing. The deposition of a thin coat of metallic nickel on the surface of the base metal enhances the adhering quality of enamels. Improved adherence tends to inhibit the formation of enamel defects such as fish scaling and copperheading (184, 90, 129, 271). If the nickel coating is too thick, enamel adherence is decreased with a corresponding increase in the formation of ahderence-type defects (229).

Enameling as a Source of Defects

Application. There are three principal methods of applying enamel slip to the base metal. These are spraying, draining, and dipping. Some defects are associated with a particular method of application; other defects are common to several application methods.

The set or consistency of the enamel must be properly controlled for each method of application, as described in "The Enamel as a Source of Defects." A high-gravity slip frequently hangs at the edges and slides off of drained pieces. Dusting may occur if a high-gravity slip is sprayed. Spraying a low-set slip may result in blown enamel, orange peel, or generally rough finishes (328, 68, 70, 83). In addition, low-set slip either sprayed, drained, or dipped may lead to double drain, run-downs, sagging and tearing (228, 190, 287, 68).

The application weight of the slip must be controlled to reduce the tendency of the coating to be defective. When the enamel is applied too thin, copperheading (74) and burn-off (228) may occur along with other defects. Thick applications of slip may lead to hairlining (102, 93, 60), lifts (53), crawling (225), tearing (138, 55), and chipping (83).

Drying. Rapid drying of the bisque coat is a frequent cause of defective enamels. A hard film is formed on the surface of the bisque coating and reduces the evaporation of water from the interior of the bisque. The water in the interior causes tearing and crawling of the coating (70, 225, 167, 55).

Materials in the drying atmosphere also produce defective coatings. Water lining is produced if there is excessive moisture in the dryer. Moisture

condenses on the part being dried and runs down the surface, removing the enamel (70). Sulfur gases present in the dryer cause scumming and pitting. As in many operations, foreign materials may cause black specks and scale (70, 230).

Firing. The firing operation frequently brings out defects in an enamel coating which are results of previous operations. However, there are also certain conditions concerning the firing step itself which can cause defects. These are overfiring, underfiring, and poor furnace atmosphere.

Overfiring (firing for too long a period or at too high a temperature) is responsible for several types of defects in enamel coatings. Too high a firing temperature may cause both the metal piece and the enamel to sag. Sagging of the enamel occurs on vertical surfaces (70) or pieces that are jarred or shaken (68). Sagging or warping of the base metal at excessively high firing temperatures may produce tearing or crawling in the unfused bisque (55, 60, 225, 138) and crazing and hairlining in the fired coat (335, 102, 227, 303, 330). A rough enamel surface with perhaps a dull finish is attributed to both too long a fire and too high a firing temperature. Such conditions also cause pinholing, pitting, and fire marking (70, 330, 218).

Overfiring produces an enamel coating which frequently is brittle and lacking in proper bubble structure. In many cases, the enamel layer contains an excessive amount of oxides formed during firing. Such an enamel may tend to fail under stress with resulting fish scaling and shiners (378, 159). Any overoxidation may lead to copperheads (60, 378, 190, 57, 151, 74).

An underfired enamel frequently has had insufficient time to adhere properly to the base metal. Adherence-type failures occur as a result of

underfiring (154). Several writers report that fracture-type defects such as fish scaling, chipping, and flaking are the results of poor adherence due to underfiring (230, 279, 229, 71, 378, 159, 267, 60, 154, 330).

The tooling which supports the piece during firing may cause enamel defects. Pin marking or star marks may occur if the piece is dropped onto a pin with such force that the bisque coat is cracked (68). Cold, heavy firing tools may cause hairlining and star marks (60).

Contaminated furnace atmosphere may lead to any number of enamel defects. Water in the furnace atmosphere is particularly harmful in that it may aid in producing hydrogen in the presence of iron. Pigskin finish, blistering, boiling, and fish scaling are all reported to be formed as a result of the moisture (14, 330, 65, 378, 68). Other gases, such as sulfur gases in the firing atmosphere, may cause scumming and pitting (230, 279, 336).

Cooling. Enamel defects that appear in a fired coating during the cooling operation are frequently functions of the rate of cooling. Rapid cooling may impose strains in the coating which cause hairlines (102), or it may be responsible for poor adherence (154, 335). Also, rapid cooling may permit the outer layer of enamel to become solid before the inner portion, and thus result in wrinkles in the coating (25).

Properly controlled cooling, described in the literature as slow cooling, tends to eliminate fish scales and shiners in fired coatings (378). Such cooling causes hydrogen to effuse from the base metal as the solubility becomes less Therefore, the gas may escape before the enamel becomes hardened and entirely impermeable. The quantity of hydrogen retained by the metal after controlled cooling may not be great enough to produce enamel defects.

IV. ENAMEL DEFECTS

Adherence Failure

Adherence failure or bond failure can be defined as the failure of the enamel to adhere sufficiently to the surface of the metal in order to stand up under normal wear. Adherence failure can be visually detected by the appearance of bright metal in the fractured area (68).

The nature of adherence and adherence failure has received considerable attention from many investigators. Writers have proposed many theories concerning the mechanism by which an enamel adheres to a metal. In general, however, there is considerable disagreement among those who have studied the subject. The principal theories of adherence mechanism are: (1) the gripping theory, which maintains that adherence is a function of metal surface roughness; (2) the dendrite theory, which maintains that tenacle-like crystals of iron become attached to the base and extend into the enamel; (3) the oxide-layer theory, which contends that enamel is bound to the base metal by means of a transition zone; and (4) the electrolytic theory, which supports the supposition that the enameling metal, relatively high in the electrochemical series, plates out from solution in the enamel, materials such as nickel or cobalt which firmly adhere to the base metal possibly through galvanic corrosion. The enamel is then mechanically bonded to the plated material. No one theory explains adherence mechanism or adherence failure.

The theories proposed suggest several factors which may either promote or lower the adherence of a given enamel-metal system. "Many factors such as the structure of the metal surface, coefficient of thermal expansion of the metal,

and ease of wetting of the surface affect the adherence of a ground coat."* In general, no one factor is responsible for adherence failure.

There are three points in particular from which adherence failures may originate. These are (1) improper preparation of the metal surface, (2) improper preparation of formulation of the enamel, and (3) improper firing procedure.

An enamel applied to a clean, roughened surface, in many instances, exhibits good bonding characteristics and little adherence failure (7, 154). However, a rough surface required by the gripping theory does not always inhibit adherence failures. This implies that other factors are involved. Nickel dipping or flashing frequently has an excellent effect on eliminating adherence failures (271, 154).

Lack of adherence of an enamel is frequently the result of improper enamel composition and/or preparation. It has been found that addition of materials, such as cobalt and nickel oxides, are quite effective in producing good adherence qualities (271, 215). These materials react with the base metal producing attractive forces between the enamel and the metal (192). However, addition of these materials does not necessarily promote adherence. Furthermore, very fine grinding of the frit has a detrimental effect on adherence (113).

The adherence of an enamel is quite sensitive to firing time, temperature, and nature of the furnace atmosphere (14, 154). Enamels that are underfired frequently exhibit an underdeveloped bond (229). Overfiring an enamel tends to increase the interfacial iron oxide layer, which may lower the adherence quality of the enamel. Both overfiring and underfiring may result in adherence failure.

*Staley, H. F., (327).

Deringer (103) in attempting to correlate the various theories of enamel adherence proposed that enamel has the same inherent adherence for iron and steel as it has for metals such as copper. He states that the difference in the adherence can be related to the behavior of hydrogen in the particular metal. Enamels applied on copper, a metal which is impermeable to hydrogen, show good adherence. Titanium-bearing steels, which limit effusion of hydrogen, also enamel satisfactorily. The author indicated that hydrogen blankets the metal during firing and prevents the enamel from wetting the metal surface. This theory is complemented by the factors previously mentioned.

An increase in adherence, with an accompanying decrease in adherence failure, could be obtained according to Deringer's theory by eliminating the hydrogen from the metal-enamel system. Operations such as roughening the metal surface, nickel flashing, and controlled oxidation all have been reported as adherence-promoting operations. These operations also tend to decrease the amount of hydrogen in the particular system.

Alligator Hide

(See Roughness.)

Bare Spots

Bare spots are spots where the ground-coat enamel does not cover the base metal adequately or where the cover coat fails to cover the ground coat. The most common cause is oil contamination on the surface. Sandblasting and pickling generally clean the metal thoroughly, but it may be recontaminated subsequently. Recontamination may be caused by contact with oil during drilling or machining operations, or even by touching the piece with bare hands.

A chronic condition of bare spots in the cover coat may be due to the ground-coat composition. If setting-up agents are used in excess, they crystallize out as the ground coat dries and forms small, black glazed places in firing. These will prevent even spreading of the cover coat, particularly if the firing temperatures are low (28).

Bare spots may also be caused by rough mechanical handling of the bisque, water breaks, or improper dipping that forms air pockets (247).

Bare spots may be eliminated by utilizing techniques which permit even spreading of the applied enamel over the piece. Proper cleaning eliminates grease and other contaminating factors on the surface which prevent even spreading. Control of the set of the slip is especially important in eliminating bare spots.

Black Specking

Enameled material exhibiting black specking, specking, flyspecking, dirt, and scale is characterized by visible specks in the enamel.

Numerous reasons have been given for the phenomenon, and it is likely that any number of things could cause specks. The most obvious and, probably, the most prevalent causes of black specks are foreign materials which may enter at any point in the enameling process and contaminate the enamel. Dirt from tools and from equipment frequently causes black specking (170). Dark particles of metal and metallic oxides which are not separated from the enamel prior to firing or which become imbedded in the surface during firing also cause black specking.

Metal exposed during firing may form black specks. Particles of oxide carried to the enamel surface in boiling or reboiling appear as black specks (190). Reboil bubbles and "glass eyes" may also give the appearance of black specks (170, 35).

Remedies for black specking are apparent from its causes (23). High standards of cleanliness of the equipment, particularly in the furnace, tend to eliminate this defect (170). Reducing the tendency of the piece to reboil and to blister also minimizes the amount of black specking.

Blistering

Blistering of enamel is the formation of comparatively large bubbles in the fired-enamel coating. The bubbles may appear as raised blisters on the surface of the fired enamel and in this condition are known by the terms blistering, blisters, boiling, boiling through, boils, and bubbling. The blister with clear enamel over the top is referred to frequently as a "glass eye." If blisters penetrate the surface of the fired enamel and do not heal over, they become open blisters, or if the remaining depressions have rounded edges, this is termed pinholes. Broken blisters which heal over and leave smooth depressions are referred to as pits.

Blistering is the result of the liberation of gases from the enamel or base metal during firing. Gases evolved from the piece during ground-coat firing produce "primary boiling." Primary boiling is in part due to the evolution of hydrogen (278, 336). It has also been shown to be partially due to carbon gases (336, 379). The phenomenon of gases being evolved from a piece during the firing of cover coats is referred to as reboiling. (See Reboiling.)

There are many other conditions which may contribute to blistering. Many of the conditions are associated with blistering in that they favor the evolution of gases during firing. The base metal is reported to contribute to this defect (80, 410, 168, 122, 346, 364, 295, 48, 132, 378). Metal preparation, particularly pickling, gives rise to blistered enamel (83, 346, 364, 201, 235, 5

The firing procedure may contribute to blistered or pinholed enamel (416, 48, 91, 14). In addition, enamels which evolve gaseous materials during firing are important sources of blistering.

Blistering may be eliminated by reducing the sources of gas evolution to a minimum. (See Fish Scaling.) However, the selection of an enamel can be made to minimize the trouble encountered from boiling, blistering, and pinholing. Since a certain amount of gas must pass through the enamel layer even under the best conditions, it is necessary to have an enamel of the proper viscosity to permit the gas to escape and still to have enough fluidity to heal over (91, 98, 28). Along with viscosity, the effect of the thickness of the enamel coating must be considered. It must neither be so thick as to stifle the passage of gases during firing nor so thin as not to seal over the holes left by the gases (91).

Bloats

Bloats seldom appear in commercial enameling operations but have been observed in laboratory experiments. They are characterized by a raised or lifted portion of an enamel at the enamel-metal interface, and they result from an accumulation of gas at the interface. They may be characterized as "lifts" or as "immature pop-offs" (79).

Blown Enamel

(See Roughness.)

Boiling

(See Blistering.)

Boiling Through

(See Blistering.)

Bond Failure

(See Adherence Failure.)

Bubbling

(See Blistering.)

Burn-Off

Burn-off is the overfiring of a localized area of an enamel coating which appears as an area of brownish-green transparent finish (228) or slaglike finish (68) in a fired coating. The areas may blend together with areas of metallic oxide (228).

Burn-off occurs in areas that have an insufficient coating of enamel. Generally, too high firing and two firings without reinforcing of the undercoated area are considered to cause the defect (246). Other factors which may contribute to the formation of burn-off are related to the set and fluidity of the slip. Too fine milling and poor draining properties of a dipped coat, which results in thickness variations of the applied coating, may result in areas subject to burn-off (246, 228).

Remedies for control of burn-off include adjusting the spray weight and pick up and specific gravity of the enamel slip. It is found that wiping pickled parts dry before dipping them also tends to eliminate burn-off (228).

Chipping

(See Fracture.)

Copperheads

Copperheads are reddish-brown spots in fired ground coats which may be seen through subsequent layers of enamel. The reddish spot indicates a localized over-oxidation of the base metal. There are two general types of copperheads:

the "raised copperhead," which is characterized by rolled edges giving the appearance of a hole or crater with reddish-brown walls, and the "depressed copperhead," which is characterized by the fact that the continuity of the enamel surface is not entirely broken, but a pit or depression is present with a brown glassy eye at the bottom (74, 68).

Copperheads may be considered to be the result of any action or disturbance producing a break in the ground coat so that oxidation of the base metal can take place (336). The disturbance is usually a gaseous condition during firing. Bubbles produced in blistering or in reboiling frequently burst and expose the base metal to the furnace atmosphere often resulting in copperheads.

Copperheading may be traced to several causes many of which may be responsible for the evolution of gases during firing. Pickling, which is known to introduce hydrogen into the base metal, may aggravate the copperheading tendency (290, 57, 89). Substances deposited on the metal or present in enamel, which break down in the firing process to form gases, can all be responsible for the defect (226, 132, 295, 74). In addition, gases present in the furnace atmosphere can contribute toward the oxidation of the base metal exposed by broken blisters in blistering and reboiling (161, 57, 321, 89, 74). Copperheading may also be traced to prolonged firing time and to the thinness of the enamel coating (226, 321, 57, 151, 371, 74).

Copperheads may be prevented by eliminating the sources of disturbance which produce breaks in the enamel during firing. Removal of gases from the metal and furnace atmosphere or controlled use of materials which produce gases during firing is important in producing enamels free from copperheads. Copperheading may also be controlled by utilizing enamels which readily "heal over"

while molten (68). In this way, exposure time of the base metal to an oxidizing atmosphere is reduced and possibly eliminated.

Cracking

(See Tearing.)

Crawling

(See Tearing.)

Crazing

Crazing is fine, almost invisible cracking, in a fired enamel coating extending down to the base metal (218, 225, 146). This defect is similar in appearance to hairlining; but, unlike hairlining, crazing may be made more visible by rubbing dirt or coloring matter over the surface (225, 68). Crazing may occur during firing or during cooling and seems to be due to differences in thermal expansion between enamel and base metal (225, 218, 146). The main cause of crazing is excessive weight of the combined coatings (371, 320); a large proportion of crazing occurs on pieces that have been rerun several times (320).

Crazing depends on the thermal resistance of the enamel. Thermal resistance may be improved by varying the composition of the enamel to produce the best enamel for a specific case--a trial and error procedure--and, to a lesser extent, by controlling the type of atmosphere in the furnace (225, 416).

In dry-process casting, crazing may be caused by stresses in the metal itself. Castings with heavy and thin sections usually show signs of crazing unless fixed by "airing" (53). Severe thermal shock may also be a cause of crazing. These types of crazing are best overcome by redesigning the metal part.

Curling

(See Tearing.)

Delayed Fish Scale

(See Fish Scaling.)

Devitrification

Devitrification is the transition of the vitreous enamel to a crystallized material which separates from the enamel, causing low gloss (68). This defect is sometimes termed fuming. The crystallization occurs when the freezing point of the enamel is in the neighborhood of the critical temperature of glass (218, 60). Devitrification is generally due to unsuitable enamel composition or melting conditions, but sometimes arises from incorrect processing conditions or treatment during use (218, 60).

Dimples

(See Pits.)

Dirt

(See Black Specking.)

Double Drain

Double drain is a redrain that occurs after normal drain of the piece is complete (68, 82). The second drain leaves an uneven enamel coating which fires improperly (82). The effects of double drain in a ground coat frequently lead to a roughness in cover coats (228).

Double drain almost always occurs in dipped or drained pieces and, usually, accompanies an overheavy application of enamel (242). The defect is a result of improper set of the slip. Slip with low-gravity and high water content frequently starts to drain the second time after the draining is apparently complete (68). Increasing the set of such a slip overcomes this difficulty.

Dummy Hole

(See Pits.)

Dusting

Dusting is a defect in the sprayed cover coat that results from the spraying of relatively dry enamel so that a wet film is not produced (68). It also may be caused by spraying at too high a pressure, by having the spray gun too far from the piece, or by having too low fluid pressure. Remedies are decreasing specific gravity and, at the same time, reducing the set of the slip and pressure of the gun. If the piece is designed in such a way that dusting occurs as a result of air turbulence around corners, the defect may be prevented by wetting the susceptible areas with a wet rag before spraying (249).

Eggshell

(See Roughness.)

Fire Marking

Fire marks are small depressions in the enamel surface caused by overfiring the enamel. These depressions resemble pinholes (218). (See Pinholes.)

Fish Scaling

Fish scale is a semicircular fracture in a fired enamel coating which may appear several months or even more after the hardened coat is formed. The fracture is characterized by a half-moon or semicircular shape. Usually, the defective areas are actually dislodged from the enamel coating, sometimes with great force. Sawai *et al.* (309) have described fish scales as having the shape of the inverted frustum of a cone and have shown that the ratio between the height and radii of large and small bases is 1:5.7:2.3, independent of the size of the fish scale and the type of enamel. Fish scales may expose bare shiny metal (317) or may extend to intermediate points within the enamel layer (182, 309, 218).

Several types of fish scales are described in the literature. Those fish scales which are apparent a short time after firing are generally referred to as "process fish scales," while those that appear a few hours, several days, or even months later are termed delayed fish scales. Shiner scales, crystallites and shiners are considered by some investigators to be microscopic fish scales (381, 218, 68, 336, 378, 159). Other writers, however, regard shiner-type defects as distinctly different from either process or delayed fish scales (368, 379, 216, 182). (See Shiners.)

Observers have indicated that fish scaling is always accompanied by the evolution of gas (368, 379, 378, 12, 79, 108, 381, 216). Motion pictures have been made of gas bubbles evolving from fish-scaling enamel surfaces to demonstrate this phenomena (11). Analyses of the gas have shown it to be almost pure hydrogen (79, 161, 378, 381, 368, 379). It has, therefore, been postulated that hydrogen collected under excessive pressure beneath a hardened ceramic coating causes fish scaling.

The thickness and coefficient of thermal expansion of the enamel, the composition and physical properties of the frit, the bond between the enamel and the base metal, the composition and processing of the base metal, and individual steps in the enameling procedure have all been correlated with fish scales. Some of the earliest writers believedthat fish scale resulted directly from the stresses created by differences in thermal contraction as the enamel and metal cooled from the firing temperatures. Others suggested that fish scale could be caused by alternate freezing and thawing of the enamel coating when exposed to moisture. However, practically all the recently published discussions agree that these factors contribute only indirectly to forming fish scale. They

either create additional hydrogen or tend to maximize the harmful effects of the hydrogen which is already present. A discussion of the phenomena of hydrogen migration in the base metal is given in "Set." Certain of the metal processes, particularly welding and pickling, have been reported as important sources of fish-scale-producing hydrogen.

Hydrogen produced in welding due to decomposition of fluxes or available in the welding atmosphere is readily dissolved in the molten metal of the weld (377). The shiny interior of blowholes in the weld metal and a porous appearance of welds made in hydrogen or ammonia atmospheres indicate the presence of a reducing gas. This gas is reported to be the cause of enamel fractures appearing preferentially over weldments (377, 378). Canfield (77) has observed that enamel over welds will frequently "fracture or shear in a semi-circular design, as though a hump had momentarily raised and suddenly fractured around the edge." Although Canfield did not report it as such, it is apparent to the authors that the pressure of hydrogen gas effusing from the welds could have caused the humps and eventual failures.

Many writers have associated fish scaling with the pickling process (153, 199, 367, 266, 378, 118, 229). It has been shown by experiment (378, 79) that the nascent hydrogen produced in acid pickling and cathodic electrolysis diffused into enameling metal. Hydrous salts formed in the pickling and neutralizing processes and deposited on the metal surface may also give rise to fish scaling (367, 336). At high temperature, these salts liberate water which, in the presence of the enameling metal, breaks down into diffusible hydrogen.

Hydrogen entering the enameling metal during the metal processing may be partially removed prior to enameling by controlled annealing. Such annealing

reduces the tendency toward fish scaling. However, an important and perhaps critical amount of hydrogen with regard to fish-scale formation is introduced into the base metal during enamel firing. This hydrogen is derived from the water driven from the enamel at firing temperatures. To demonstrate that water from the enamel is responsible for defects, Kerstan (186, 185) prepared a ground coat slip with ethyl alcohol instead of water and applied it to a steel which was susceptible to fish scaling. No fish scales appeared in 20 days.

Water present in the enamel is derived from the milling water, the quenching water, the dissolved water in the frit, and the chemically combined water in the clay (420, 270). Moore et al. (270) conducted deuterium tracer experiments and were able to deduce that of the sources studied the water dissolved in the frit was the most important source of the defect-producing hydrogen. Water driven from the enamel at the metal-enamel interface reacts with the iron and may also become dissociated through galvanic action to produce nascent hydrogen, which is readily absorbed by the metal at firing temperature. Iron oxides, which form the so-called hazy layer in the enamel coating, are also formed.

If hydrogen is not allowed to enter the base metal, fish scaling may be reduced. Zapffe (378, 420) showed that hydrogen is not introduced into cast iron during enamel firing as it is into steel. The hydrogen released encounters carbon in the surface of the iron, forms insoluble methane, and escapes through the molten enamel. This writer indicated that the tendency for cast iron to fish scale is less than that of steel. Enameled metals which are impermeable to hydrogen do not fish scale (105). Investigators have shown that by preoxidizing steel in a controlled atmosphere, a barrier layer of oxide is formed which is impermeable to the water released from the enamel during firing (380,

159). Preoxidized plates are shown to exhibit no fish scaling even when fired at a high dew point. However, those not oxidized, fired in moist air, fish scale rapidly (159).

Hydrogen (in the atomic state) once retained in the base metal during any of several actions will effuse slowly from the metal at room temperature if provided with sufficient driving force. An enamel coating is likely to be less permeable to hydrogen than the metal is and, therefore, acts as a barrier to the effusing hydrogen. The enamel may also provide isolated voids at the metal-enamel interface in which molecular hydrogen becomes occluded. If the pressure of effusing and/or occluded hydrogen at the interface or at any intermediate level in the enamel layer exceeds the enamel and bond strength at any point, a rupture will occur. Fish scales are sometimes formed by such force that when the break occurs the enamel is exploded from the coating.

Fish scaling may be prevented if the hydrogen trapped within the boundaries of a metal piece is dispersed to such an extent that critical pressures (critical pressure may be considered to be the minimum gas pressure required to fracture a given enamel) never exist. Several observations in the literature substantiate this fact. Steel pieces enameled on only one side, the opposite side open to effusing hydrogen, fish scale less readily than do pieces enameled on both sides (378, 159). Enamel coatings with good bubble structure (many bubbles dispersed in the one-mil layer adjacent to the metal (59) dissipate the hydrogen pressure and show less fish scaling than do glassy coatings with poor or no bubble structure (159, 216, 182, 199, 63). Cold working has been reported to open the grain structure of the metal, allowing hydrogen to effuse more easily and rapidly from the piece during firing and cooling, ridding the piece of

hydrogen (378, 159, 368), or allowing hydrogen to become trapped in discontinuities and unable to effuse at room temperature. This is substantiated in that sandblasted pieces are known to fish scale less than enamels on unprepared surfaces (378, 159). Sandblasting may be regarded as a mild form of cold work.

The tendency of an enamel applied to a metal piece to fish scale appears to be related to the thickness of the metal which in turn is related to the relative amount of hydrogen retained during firing or the ability of the hydrogen to effuse after firing. Thin metal sheets have less tendency to fish scale than thick sheets of the same metal for a given enamel application (378, 317). This conforms with the fact that the amount of hydrogen which diffuses in a given time through a metal decreases with increasing thickness of the metal (378). Thin sheets may well lose hydrogen in such quantities at elevated temperatures during the cooling process that the pressure of the remaining hydrogen is insufficient to produce fish scales. Thick sheets, however, may retain hydrogen which does not have time to leave the steel during cooling and which may eventually exert sufficient pressure on the hardened coating to produce fish scales. In apparent contrast to this analysis, observers have noted that fish scales appear over thin sections of enameled plate and not over thicker sections of the same piece. Deringer stated that more fish scaling would be encountered in hot-rolled stock from 1/8-inch to 1/4-inch thick than in thicker stock. It appears that hydrogen enters steel during firing at a constant rate regardless of the plate thickness. Hence, Deringer concluded that the pressure of the hydrogen would be a function of the plate volume in which it was dispersed. It appears in this case that the thick

homogeneous plate is capable of dispersing the hydrogen within its structure so that the pressure of the gas at the interface may never be critical.

The composition of frit and the resulting structure of fired enamel are responsible for fish scales under certain conditions. Klärding (195) has demonstrated that a given metal enameled with several different enamels exhibits varying fish-scaling tendencies. It is obvious from the previous discussion that water- and hydrogen-bearing materials of the enamel make-up are potential sources of fish-scale-producing hydrogen. Clays, although possible sources of defects because of chemically combined water have been shown to impart the important pressure-dissipating bubble structure to the fired enamel. Fish scaling occurs more readily in enamels containing "clear-firing" clays (those associated with poor bubble structure) (159, 59). These clays are known to have a greater amount of combined water than opaque clays and to produce glassy enamels with poor bubble structure. The clays which impart the desirable structure to enamels and are associated with improved fish-scale resistance appear to be rich in absorbed organic material. Higgins demonstrated that mill additions of certain organic substances, such as methylene blue, improved the structure of the fired enamel even when "clear-firing" clays were used (159) and was sufficient to eliminate fish scaling. He pointed out, however, that the addition was not practical from a shop standpoint and that further work should be undertaken along these lines. Addition of highly refractory porous materials to the mill also reduces fish scaling by controlling the structure of the fired enamel (367, 379, 368, 127). The enamel may be made more permeable so that the diffusion coefficient of enamel with regard to hydrogen would approach the diffusion coefficient in metal.

Excess amounts of material such as iron oxides formed in the enamel during prolonged firing tend to fine out or eliminate the bubbles structure (159), consequently reducing the fish-scale resistance.

Enamelers have reported a number of enamel-processing factors as causes of fish scales. Some of the factors were associated with fish scaling before general acceptance of the hydrogen theory and may or may not have any relation to hydrogen behavior. Both overfiring and underfiring give rise to fish scaling and bear a definite relation to hydrogen behavior. Overfiring tends to eliminate the bubble structure and reduce the strength of the fired coat (190, 378). Overfiring may cause the enamel layer to glaze and become more impervious to effusing hydrogen. On the other hand, insufficient bond and enamel strength is developed in underfired coats, and less hydrogen pressure is required to rupture the enamel. In addition, observers report that faulty furnaces with contaminated atmospheres (66, 144, 150, 153, 175, 199, 367, 60), oversmelting (153, 199, 266), and failure to stir the ground coat slip are all associated with fish scaling.

Many writers, especially those writing before there was general acceptance of the "hydrogen theory" of fish-scale formation, indicated that fish scales were the result of stresses developed in the enamel (190, 302, 320). However, there is little experimental evidence to substantiate this thinking. Strains are reportedly present in fired enamel coats because of the difference in thermal coefficient of expansion of the enamel and the base metal or even because of the expansion gradient through the enamel layer. Fiebig (118) prepared several enamels and determined their coefficients of expansion. Applied on thick metal containers, the enamel with the lowest coefficient of expansion exhibited the least amount of fish-scale formation. Kautz (379, 368) had indicated that

enamels fired on metals are under compression and that the compressive stresses together with weak adherence may contribute to fish scaling. Patrick (277), Hughes et al. (171) have observed fish-scalelike spalls occurring in cover-coat enamels on surfaces subjected to alternate freezing and thawing in the presence of moisture. An open blister showing rust was always found in the area of the defect. It was suggested that water enters a bubble in the enamel and freezes. The resulting stresses could then be such that the fish-scalelike defect would occur. The writers did not consider the possibility of hydrogen formation resulting from the rusting in the vicinity of the defect. The authors of this report do not know whether this defect was fish scale or a separate phenomenon.

It appears that an enamel which adheres tenaciously to a metal is more likely to resist the pressure of hydrogen at the interface of metal and to be more fish-scale resistant than coatings demonstrating poor adherence. The question of the relation between adherence and fish scaling of enamels is not settled. Moore (271) and others (90) indicate an apparent relation in that adherence-promoting nickel dip reduces the tendency of certain enamels to fish scale. Zapffe (375) explains that hydrogen evolved during firing acts as a barrier between the base metal and the enamel. The gas blankets the metal surface and prevents the enamel from wetting the surface and adhering to it. Martin (216, 217) states that with fish scaling the lack of bond is usually obvious since the piece will usually show excessive areas of bright metal when tested for adherence. On the other hand, Bowman (63) in conducting Porcelain Enamel Institute adherence tests on several enamels having different degrees of fish-scale resistance found that there was no apparent correlation between fish scaling and adherence.

Observers have found that the tendency of an enamel-metal system to fish scale is related to the characteristics of the base metal. Deringer (105), Bowman (63), and others conducted experiments in which enamels were fired on a series of metals and found that each metal fired with a given enamel showed different fish-scaling characteristics. It was noted, as has already been pointed out, that the characteristics of the metal responsible for fish-scale formation are in general functions of the hydrogen relationship to the particular metal. Enameled metals relatively impermeable to hydrogen such as stainless steels, chrome steels, copper, and gold do not fish scale. Cast iron, high-carbon steels, and other metals which contain materials that will react with hydrogen or impede the progress of diffusing hydrogen are less likely to fish scale. Tests indicate that case iron continually loses hydrogen at elevated temperatures (decarburizing action) and that the presence of carbon prevents further hydrogen absorption. Zapffe (375) has shown that certain alloying elements added to steel will improve its enameling qualities. In particular, he noted titanium and chromium have this quality in that they apparently tend to decrease the rate of hydrogen diffusion. He explained the action as reverse catalytic or poisoning action on the diffusion or as a "plugging of the gaps" in the crystal lattice by the alloying element.

Segregated impurities in metals such as slag inclusions have been reported as being responsible for fish scaling. These impurities are heterogeneities in and surrounding which molecular hydrogen becomes trapped or stored. They may also be materials with which hydrogen reacts chemically to form more or less stable compounds. Diffusion of this combined hydrogen into the metal surrounding the inclusion and possibly to the surface above the inclusion takes place

on heating above the dissociation temperature of molecular hydrogen or that of the particular compound. The hydrogen effusing at the surface above such impurities, being more concentrated than that at other sections, could cause isolated fracture in the enamel. Zapffe (378) introduced artificially into steel certain segregated impurities and observed that hydrogen-caused defects occur preferentially over sections containing the impurities. Other gases released from the metal or from included compounds in the metal, even in small quantities, may also contributeto the gas pressure at any point. The gases other than hydrogen which could contribute to the pressure are carbon dioxide, carbon monoxide, methane, nitrogen, and water (336). These gases should be considered in fish-scale analysis, but they are generally relatively unimportant.

Various operations have been suggested as remedies for the fish scaling of enamels on steel. Even though there are many factors that may be considered in fish-scale analyses, the problem of preventing their occurrence can be simplified to one of reducing the hydrogen pressure to a value lower than that found to be critical for the given enamel-metal combination. In general, these operations reduce the quantity of hydrogen available in the base metal and bisque coat prior to firing, produce conditions which prevent absorption of additional hydrogen by the base metal during firing, or in some way produce conditions which minimize the effects of the pressure of the hydrogen which effuses from the fired piece.

The initial quantities of hydrogen or sources of hydrogen in the enameling materials should be reduced as much as possible. Hydrogen retained by the base metal prior to firing can be kept to a minimum by reducing the pickling and by preventing rusting (378, 375). Cold working the surface followed by controlled

annealing tends to reduce the quantity of hydrogen retained by the metal or to reduce the effusion at room temperature. Shot peening is particularly recommended. The annealing temperature should be such that the rate of hydrogen effusion is maximum. Hydrogen- and water-bearing enamel materials should be kept to a minimum so that the gas is not introduced into the metal during firing. It is also necessary that the bisque coat and the furnace atmosphere be thoroughly dry so that water is not available during firing. It has been suggested that preheating the bisque-coated piece at an elevated temperature drives out the water before the high firing temperature is reached. The temperature should not be so high that the solution of hydrogen is excessive.

Several operations may be performed which tend to prevent additional hydrogen from entering and being retained by the base metal during firing and, thereby, eliminate fish scaling. Preoxidized base metal has this characteristic (380, 375). A well-formed, tightly adhering oxide scale appears to prevent water driven from the enamel during firing from reaching the hot surface of the base metal. Nickel dipping also appears to reduce fish scaling in that the nickel layer reduces the amount of hydrogen retained by the metal. The nickel also promotes adherence, which apparently further decreases the tendency of the enamel to fish scale.

The effects of the pressure of hydrogen may be minimized in several ways. Use of opaque clays and organic mill additions produces a bubble structure, which dissipates the hydrogen pressure at the metal-enamel interface. The addition of refractory materials to the enamel gives rise to a relatively porous enamel which may permit hydrogen to effuse from the piece during firing (367, 379, 127).

Flaking

(See Fracture.)

Flyspecks

(See Black Specking.)

Fracture

A fracture is the spalling or breaking of the fired enamel coating with platelike pieces of various sizes being removed. Fractures, often termed chips, chipping, flaking, and spontaneous fractures occur on edges, corners, rounded areas, and over welds and seams. Spontaneous fractures at a rounded area or edge are generally termed flaking.

Zapffe (381) suggests that fracture-type defects are formed by the evolution of hydrogen gas from the base metal. (See Fish Scaling.) He further states that the difference in appearance of fracture-type defects (including fish scales) principally depend on "differences in the physical properties of the enamel, the metal-enamel bond, and the rate, quantity, and localization of the hydrogen effusion."

Other factors that may cause fractures directly or maximize the action of hydrogen are manifold. All of the following have been reported as causes: overheavy enamel application (224, 138, 3, 45, 163); improper design, i.e., some parts of a piece much thicker than others (224, 138, 3, 45, 318); careless handling, both on the assembly line and in shipping (224, 45); faulty welding (224, 201); improper enamel composition (224, 138, 3, 45, 77); and poor firing technique (224, 138, 3, 45, 338).

Eliminating hydrogen from the enamel-metal system reduces the tendency of an enamel to fracture (381). Care in the design and preparation of the

piece to be enameled can also eliminate many causes of fractures (224, 138, 3, 45, 318, 163, 338).

Fracture, Spontaneous

(See Fracture.)

Fuming

(See Devitrification.)

Glass Eyes

Large bubbles or blisters with clear glass over the top are called glass-eyes. (See Blistering.)

Hairlines

Hairlines are lines of color or depression in the fired surface of the enamel cover coat. The line follows the same kind of pattern as glass fractures, but dirt will not smudge into hairlines as it will in craze lines (68). Hairlines usually appear as fine, black lines. They are actually lines of ground coat penetrating up into the cover coat (168) and appear only after the firing of the cover coat (11).

In general, this defect is caused by the cracking of the fired ground coat and bisque cover coat before melting of the cover coat (254, 168). If the metal specimen becomes distorted, stresses may develop and cause the gound coat to crack, which in turn causes the cover coat to crack. The molten ground coat is then drawn up into the cover-coat cracks by surface tension of the glass. Hairline formation ends when the enamel surface becomes smooth and continuous (93).

Experimentally, hairlines have been produced by shadowing part of the piece during firing (330), conducting heat away from part of the piece during

firing (335), and bending the piece after ground-coat firing (190). The most common causes of hairlining seem to be "cold spots," caused by heat loss by radiation or conduction during firing to nearby cold objects (11).

The condition of the ground coat is an important factor in hairlining. Applying a hard enamel over a soft ground coat may cause hairlining because of fluxing of the ground coat before the cover coat (52). Underfiring of the ground coat may cause hairlines, and it may be caused by too low firing temperatures, firing for too short time, or too thick ground coat. Where pieces have thin and thick sections, it may be necessary to take precautions to avoid overfiring thin sections while firing thick sections sufficiently to prevent hairlining (11).

Drying at too high temperatures may form a crust on the surface of the bisque, thus sealing in moisture which will cause cracks in the bisque and hairline on firing.

Any distortion or flexure of the piece during the early stages of firing, whether due to weakness of weld (77, 168), differential thermal expansion or improper support in the furnace (254), is likely to cause hairlines. Such effects can be avoided by carefully designing parts or by controlling conditions of firing (102, 93). It is important to use a base metal that will not sag (102). Hairlining in steel pieces that have been subjected to difficult forming operations might be avoided by annealing the pieces after forming (139).

In general, hairlining, like crazing, is a result of low thermal resistance of the enamel (114). More refractory ground-coat formulas are helpful in this respect. Thermal resistance is affected also by the type of atmosphere in the firing furnace (416). Another important factor is the ability of the finish

coat to heal over after cracking. This property is dependent on surface tension (335), fluidity (335), and film strength (102). A dense bubble structure in the ground coat is also helpful in preventing hairlining (93, 102).

Honeycombing

(See Spongy Enamel.)

Jumpers

Jumpers, pop-offs, and poppers are terms used to describe fracture-type defects that develop in a cover-coat bisque. The fractures occur as an explosive detachment of fragments of enamel from the surface (226, 29, 114, 330). The fracture may either expose bare metal (226, 330) or expose the underlying ground coat (226, 29, 114).

The defect is generally attributed to a failure of the fired ground coat which disrupts the bisque cover coating (336). Failures of the ground coat are particularly prevalent during drying or in the early stages of the firing process. The increase in temperature accompanying these processes enhances the effusion of hydrogen from the base metal. Hydrogen pressure increases at the metal-enamel interface and may become sufficient to produce failure of the fired coating. Failure in the ground coat of this type, which produces jumpers, is essentially delayed fish scaling, with the delay period being shortened by the rise in temperatures (336).

The formation of jumpers and poppers may be prevented in the same ways that fish scaling and fracturing are prevented. (See Fish Scale.)

Knobs

(See Lumps.)

Leather Finish

(See Roughness.)

Lifting (Lifts)

A lift refers to a visible separation of the enamel layer from the underlying metal. The lifts are formed by gas pockets of hydrogen that form between the metal surface and the enamel layer (270). This defect could, of course, be prevented by controlling the evolution of hydrogen from the enamel and metal, and by use of enamels having good bonding characteristics (215, 98, 68, 375, 304, 75). (See also Fish Scaling and Blistering.)

Lumps

Lumps, pimples, and knobs are terms which describe a defect characterized by small bumps on the surface of the finished ware. There are two primary causes for this defect. It may be caused by the presence of foreign matter under the enamel or to large particles in the milled enamel. In either case, the only remedy is to control the process more closely (53, 288, 330).

Opening

(See Tearing.)

Orange Peel

(See Roughness.)

Overfire

An overfired enamel appears as a dull and possibly pitted surface and results from firing for too long a time or at too high temperature (68). An undesired result of overfiring is the elimination of the bubble structure in the enamel and the saturation of the enamel layer with iron oxide (271, 272). The resultant glassy enamel is impermeable to hydrogen and possibly weakened to a point considered critical in the formation of other defects.

Obviously, production of overfired enameled metal surfaces is prevented by proper control of firing. (See also Roughness.)

Pigskin Finish

(See Roughness.)

Pimples

(See Lumps.)

Pinholes

(See Blistering.)

Pin Marking

During the firing process, the metal is supported in the furnace at various points. When the load is unevenly distributed, the under surface of the sheet metal is distorted by the points carrying the heavier load. The distortions are called pin marks. They can be eliminated by increasing the number of support points, by grinding the points until the supporting surfaces all lie in one plane, by preheating the points, by firing at a lower temperature, and by using a sheet metal whose warp and sag resistance is high (259).

Pits

Pits are defined as smooth, well-covered depressions in the fused enamel surface, somewhat larger than pinholes (218). They are conelike depressions in the surface of the fired cover coat (369, 255).

Pits may be caused by contamination of the enamel by low-melting material (288, 369), excessive soluble salts leached from the frit during milling, contamination of a hard enamel by softer frits (255), or contamination of one kind of enamel coating with another (288). Underfiring, overfiring, or the breaking down of copperheads during firing the cover coat may cause pits, as well as sulfur pock marks caused by sulfur dioxide in the furnace (14).

Since pitting is usually the result of contamination, careful process control is the best remedy (288, 216, 217, 230, 190). Pitting which is the result of gaseous matter being liberated from the metal during firing may be regarded as another form of blistering (288, 216, 230, 190).

Pop-off (Poppers)

(See Jumpers.)

Pull Through (Stipple)

Half-concealed gas-caused bubbles and fine specks of well-distributed carbon appearing in single-coat white enamel are sometimes referred to as pull through or stipple (65).

Reboiling

Reboiling is a disturbance of the fired ground coat characterized by the sudden appearance of blisters in the ground coat. The blisters appear during the heating period in the second or subsequent firing. Frequently, the blisters subside and disappear as the firing temperature is increased or the firing time extended (183). The defect may appear as a black speck in the underlying enamel or may appear as a roughened surface, sometimes termed pigskin or alligator hide (336).

Numerous studies (270, 103, 269, 100) have shown that the cause of reboiling is the evolution of hydrogen gas. The hydrogen evolved is primarily the gas absorbed during previous firings, but there is some controversy on this point (87, 209, 79). However, the behavior of hydrogen at elevated temperatures gives the only satisfactory explanation of the frequent subsiding and disappearance of blisters during extended firing or upon increasing the firing temperature. The effusing hydrogen which forms the blisters during firing redissolves in the base metal and allows the blister to subside.

Other suggested causes of reboiling are related to the ground enamel (16, 304, 113, 78, 155, 100), base metal (375, 105, 108, 155, 12, 118), preparation of the base metal for enameling (375, 75, 380, 155, 12), the thickness of the ground coat (183, 170, 154), rates of heating and cooling in the furnace, and the composition of the furnace atmosphere (16, 170, 154).

The tendency of an enamel to reboil can be reduced in the same manner that the tendency to fish scale is reduced. (See Fish Scaling.)

Ripple Finish

(See Roughness.)

Rollback

(See Tearing.)

Rolling

(See Tearing.)

Roughness

Roughened enamel coatings have been described by several characteristic terms. Alligator hide, blown enamel, eggshell, leather finish, orange peel, pigskin, rippled finish, ruffled ground coat, sandpaper finish,and wrinkles are used to describe various forms of roughness.

There are two primary causes of a rough enamel finish. The method and quality of the application is one and improper firing is the other.

Blown enamel, orange peel, rippled finish, and wrinkles are generally the result of faulty application techniques (68, 165, 328, 320). Ridges in the enamel surface and a segregation of particles of the enamel occur if the set of the slip is too low. Attempts to spray a very wet slip commonly give rise to these finishes. Spraying at too high a pressure or holding the gun too close to the piece may produce the same characteristic finishes.

Improper firing or conditions that arise during the firing operations cause roughened conditions referred to as alligator hide, eggshell, leather finish, pigskin, ruffled ground coat, and sandpaper finish (251, 68, 14, 416, 88). Overfiring, in particular, causes the defects. A rough enamel surface occurs when the enamel is fired with an insufficient quantity of oxygen (14, 416). Enamels fired in a pure nitrogen or carbon dioxide atmosphere are subject to the defective finish. Firing in moist atmospheres produces blistering which may lead to a roughened surface frequently termed pigskin finish.

Gases evolving from the piece during firing may produce small bubbles in the enamel which give the surface an eggshell or pigskin finish. The pressure exerted by the gas raises the surface of the coating sufficiently to give it a rough texture. Large reboil bubbles in subsiding may produce ridges in the molten enamel which remain in the hardened coat. This condition is termed alligator hide, leather finish, or pigskin finish (68).

Poor surfaces of the enamel coating may be prevented by improving both spraying and firing techniques. The proper adjustment of the spray gun and enamel set are all important in producing a smooth coating. The set of the slip must be such that the spray is wet enough to produce a satisfactory fired finish, yet dry enough to prevent excessive roughening of the enamel from the force of the spray. The thickness of the applied coating must be kept to a minimum to prevent rippling of the enamel or sagging of the surface. (See Sagging.)

Gas evolution and contaminating gases in the firing atmosphere must be kept to a minimum to avoid blistering of the enamel with resulting roughness. The control of gas evolution is discussed under fish scaling.

Ruffled Ground Coat

(See Roughness.)

Sagging

Sagging, or "run-down" (218), is the forming, upon firing, of an excessive amount of enamel in one place usually in the form of a ridge or a run resembling a tear drop. Sagging produces a roughness which is similar in appearance to orange peel (70) or rippling (260) and is formed when the enamel slides into patterns down vertical surfaces during firing (228, 68). Sagging may be differentiated from rippling in that enamel which is rippled during spraying improves with increased firing, while sagging, which may also originate with spraying, becomes worse with increased firing (260).

Causes of sagging are heavy application of enamel, too high a firing temperature, and jarring of the piece when at high temperature in the furnace. Roughness in the base metal or in the applied enamel will tend to exaggerate sagging (70).

Although sagging is more apparent in fired cover coats, the ability to resist sagging is mainly dependent upon the ability of the underlying ground coat to resist sag. Excessive neutralizer deposition on the ware may promote sag by causing variation in the pickup during dipping and also by lowering the fusing point of the ground coat (228).

Remedies include using a shorter and hotter fire, reducing the weight of ground coat and/or cover coat, eliminating excess water vapor in the furnace, changing composition of the slip to reduce the tendency to oxidize and to give bubble structure, and, where possible, firing pieces horizontally. Spray sagging, identical in appearance to sagging, can occur along scratches and stone

marks in the ground coat when the cover coat is sprayed on with the piece in a vertical position. It is remedied by using a drier spray or by spot spraying a very small amount of spray over the scratched area, allowing it to dry, and, then, spraying the entire piece in the normal manner (260). (See Roughness.)

Sandpaper Finish

(See Roughness.)

Scale

(See Black Specking.)

Scarred

Scarred or scarred finish is a mark in the fired enamel surface produced by firing enamel which was scarred after drying (68). The term is also applied to the defect in the dried bisque, either undercoat or cover coat (244).

One cause is the movement of ware on the conveyor while still in the drier or when taken off the conveyor. Another cause is too soft a bisque coat, that is, a bisque that will rub off when handled. This difficulty is remedied by increasing the heat in the drier and by the addition of clays, bentonites, gum, and sodium alginates (244).

Scratch Blisters

This defect can be defined as the appearance of blisters and bubbles in the enamel over scratches in the metal surface. Blistering is caused by preferential effusion of hydrogen from the scratch. Scratching of the metal surface apparently cold works the area which enhances hydrogen effusion (378). The type of scale present on enameling iron exerts a controlling influence, in the degree of blistering as does the geometry of the scratch and the degree of cold working of the steel. Scratch blisters may also be caused by gases evolved from impurities or from precipitated salts trapped in the scratch (374). (See also Blistering.)

Scuffed

(See Scarred.)

Scumming

Scumming is the formation of dull areas (230), white deposits, or poor glass (218) on the surface of enamel during or after firing (218), resulting in low gloss or changed color (68). The defect may be small (68) or cover the entire surface (230).

Scumming due to the presence of sulfur gases or sulfates in the system is called sulfate scumming (279, 260). Sulfate scum is easily recognized by its color, taste, and solubility in water. Sulfate scumming is remedied by preventing leakage of sulfur gases into the furnace, by reducing or eliminating electrolytes which contain the sulfate radical, and by packing or storing ware in an atmosphere as free as possible from sulfur gases (279, 230).

Scumming due to improper firing is called "underfire scumming" (279). It can be corrected by refiring, or it can be avoided by reducing the amount of clay or opacifier, by finer grinding, and by using an opacifier that is low in total soluble material (279).

Causes of scumming may include such factors as these: the reaction of components of the enamel with each other (218), the separation of soluble matter on the surface (218), improper aging of milled enamels (369), and incorrect suspension of clay in the slip (60).

Remedies suggested for scumming are raising the specific gravity of the spray and adding hydrochloric acid to the mill (260).

Shiners

Shiners, shiner scale, or crystallites are synonomous terms used to describe minute fractures which appear in fired ground coats. The microscopic

fractures are often recognized as a uniform glittering of the enamel due to the reflection of light from their smooth surfaces. J. H. Keeler et al. (182) have described a shiner as a small conchoidal crack intersecting the surface of the enamel but not resulting in an ejection of a fragment from the surface.

Many writers have indicated that shiners are nothing more than minute fish scales and as such are caused basically by hydrogen. Zapffe and Yarne (381) have examined shiners under the microscope and have prepared photographs of these fractures to show that they are similar in appearance to the true fish scale. These writers have shown that shiners are generally associated with a highly developed interfacial oxide layer and a thin coat, both of which may result from overfiring. They have related the size of the shiner to the thickness of the coat. Thick coats on a given metal exhibited large shiners (fish scales) while thinly coated specimens developed uniform small shiners. The difference in appearance of these apparently similar fractures depends primarily on differences in the properties of the enamel and its relation to the metal and in the nature of hydrogen effusion.

Some writers hold that shiners are not caused by hydrogen pressure and that the defect is distinctly different from fish scaling. Kautz (368, 379) indicates that the defect is caused by overfiring and by saturation of the enamel layer with iron oxides. Keeler et al. point out that although shiners are generally indistinguishable from small fish scales when viewed with the unaided eye, the differences between the two are readily observable at 5 to 20 X. These writers maintain that shiners result from stress in the enamel coating.

These seemingly anomalous findings concerning the cause of shiners may actually support the hydrogen-effusion idea. Shiners are not always associated

with overfiring for Zapffe (381) has reported that the defect has been found in normally fired articles. He points out that overfiring is not essential to the formation of shiners but is an important contributing factor. Overfiring tends to reduce the thickness and bubble structure of the fired coating to a point where even low hydrogen pressure may produce ruptures.

Shiners found on thin sheets and sheets coated on only one side where the larger size fish scales are not normally found apparently demonstrate the fact that less hydrogen is required to cause shiners than to form fish scales. Zapffe and Yarne (381) have proposed that the amount and pressure of hydrogen considered critical in the formation of shiners may differ from that required to produce fish scales because of differences in the particular enamels and hydrogen behavior associated with the system.

The remedies for shiners are essentially the same as those listed for fish scales. In general, the defect may be eliminated by controlling the means by which hydrogen is introduced into the system, effectively reducing the hydrogen available below the critical amount. Kautz (368) reports that the application of heavier coats, reduction of heat treatment, and control of oxidation at the enamel-metal interface during firing has eliminated shiners in practice. Control of firing and controlled preoxidation of the base metal also tend to eliminate shiners (380, 159). (See Fish Scaling.)

Shivering

(See Sliding and Sagging.)

Shore Lines

Shore lines are characteristic colored or depressed rings or lines in the fired enamel surface. The defect is confined primarily to acid-resisting enamels (218, 254).

Shore lines form as a result of too rapid drying or unsuitable setting up of the enamel (218) and precipitation of salts such as sulfates (68).

This defect is reportedly remedied by increasing the set, by reducing the water content of the slip, and by spraying as dry as possible (254).

Sliding

Sliding and shivering appear to be a form of sagging (68, 344). The defect is caused by improper flow of enamel during draining which may be the result of too fine grinding (88). (See also Sagging.)

Spalling

(See Fracture and Thermal-Shock Failure.)

Specking

(See Black Specking.)

Splotches

Splotches, like bloats, appear more frequently under laboratory conditions than in commercial practice. They are defined as areas of separation developing at the steel-enamel interface under a transparent enamel. In many splotches, optical interference fringes can be observed at low magnification. Splotches are very similar to bloats in their causes and properties (79).

Bloats and splotches in general appear only after the piece has been fired and cooled, sometimes long after the firing cycle (80).

Spongy Enamel

Spongy enamel is a fired enamel coating that is full of excessively large bubbles. This bubble structure produces a weak coat which is susceptible to the action of several enamel defect-producing mechanisms.

In general, this defect is attributed to gases produced during firing or present in the furnace atmosphere. Excess carbon dioxide and fuel gas in the

furnace atmosphere have been found to produce spongy enamel in practice (311, 416, 248). Heavy ground coats and underfiring have also produced this defect (248). Some clays will produce an excessive number of bubbles in the fired coating.

This condition may be controlled by selection of proper clays and other components of the enamel, by proper firing and by reducing the sources of gas evolution which give rise to the bubbles.

Star Marks

Star mark is a term referring to characteristic lines or cracks radiating from a point. These marks are generally found on the opposite side from firing pins. These marks are caused by impact with a sharp object prior to firing, e.g., the covered piece may be dropped on the pins (82,60, 68). Care in handling is sufficient to prevent this defect.

Steel Lines

Steel lines are lines, visible in the enamel surface, which follow the rolling direction of the steel. These lines may result from scratches in the metal surface (68).

Stone Marks

Stone marks are marks resulting from the stoning out of enamel defects. These marks are prevented by use of proper stoning techniques (259).

Strainlining

(See Hairlines.)

Tearing

Tearing is a separation-type defect commonly found in cover coats (225, 320, 216, 217) and occasionally found in ground coats (216, 217, 68). The defect

is distinguished by minute breaks, cracks or tears in a fired cover coat (225), or by a pattern of the undercoat enamel or metal showing through the coating. This characteristic pattern appears similar to the pattern of tearing in cloth (68).

Tearing may occur particularly as a result of breaking or cracking of the enamel during drying and firing. The enamel at the crack pulls away from the metal or from an undercoat during firing and fails to fuse together (218, 216, 217, 320, 11). Moving pictures demonstrate that cracks form in the bisque in the early stages of firing (11). The cracks widen and lengthen with shrinking of the enamel, peeling up and rolling back at the edges. The rolling back of the enamel coating during firing is sometimes referred to as "curling" (344).

Tearing may be severe and, as such, is referred to as "crawling" (225, 218, 68). In this situation, the layer of enamel tears away during firing to aggregate as a series of patches or islands. The ground coat or only a thin layer of enamel remains between the islands. Crawling or severe tearing is sometimes termed "opening" (218) and "rollback" (68).

Tearing (crawling, curling, opening, or rollback) is attributed to various causes. As was mentioned, the defect is frequently derived from cracks in the bisque coating (283, 11). Cracks and subsequent tearing result from overheavy applications, rough handling of the coated piece, too rapid drying, too finely ground enamel, enamel with too high melting point, and bisque with poor film strength (252, 320, 136, 60, 225, 218, 68). Tearing or crawling may also occur as a result of improperly cleaned surfaces. Enamel pulls away or rolls back over dirt or grease (68) with resulting tears.

Care in handling and processing reduces the tendency of enamel coatings to crack and tear. Slower drying at lower temperatures and more complete drying help eliminate tearing (320). Lower melting enamels tend to prevent tearing (320, 283, 306). Also complete cleaning of both metal and ground coat reduce the tendency of the enamel to tear or crawl (216, 217).

The degree of tearing may be considered to depend upon the surface tension of the molten enamel and the extent to which it flows as a result of firing. The use of mill additions which provide a low surface tension insures a minimum of rolling back at cracks in the coating (335). Additions to produce high fluidity of the molten enamel tend to give rise to maximum healing of the tears.

Tension Cracks

(See Crazing.)

Thermal-Shock Failure

Thermal-shock failure is the fracturing, spalling, or crazing of a fired enamel produced by sudden cooling or heating of the enameled surface. Enamel failures associated with the alternate freezing and thawing of a liquid in contact with the enamel are termed spalls, or freeze-thaw spalls. Freeze-thaw spalls are further described as crater spalls which are shaped like an inverted cone with a bubble at the apex; fish-scale spalls which are similar in appearance to fish scales (171) (see Fish Scaling); and linear spalls associated with fine scratches on the enamel surface (277). These spalls are considered to be large spalls if they are caused by blisters of diameter greater than the thickness of the cover coat, and small spalls if caused by blisters which are small compared to the cover-coat thickness (277).

The expansion of the enamel as it is related to the expansion of the steel is one of the major factors affecting mechanical and thermal-shock failure (21). If the thermal coefficient of expansion of the enamel differs greatly from that of the base metal, strains are imposed on the enamel during rapid changes of temperature which may result in enamel failure.

Freeze-thaw spalling appears to depend upon the presence of moisture, temperature fluctuations above and below freezing, and improper bubble structure of the enamel (277, 171). Bubbles close to the enamel surface apparently permit moisture to enter (171). At freezing temperatures, the moisture freezes and expands, exerting a force capable of rupturing the enamel. This idea is supported by the fact that an increase in the number of bubbles per unit area tends to increase the number of spalls (277, 171).

An entirely different type of spalling is produced by baking of thick syrup on the surface of the enamel, as often happens in cooking ovens (319). Experimentally, this effect is produced only when the syrup is thick and not watery. The gauge and composition of the base metal has no effect on this type of spalling; nonferrous metals, stainless steel, and carbon steel all act alike. Enamels with a low coefficient of thermal expansion resist this type of spalling best.

A possible explanation of this type of spalling is that the syrup at elevated temperatures forms bubbles, which, being poor conductors of heat, permit the enamel adjacent to the bubbles to become very hot in small areas, thus producing local thermal shock (319).

Experimental data indicate that as the expansivity of the enamel decreases, resistance to thermal shock increases on flat surfaces. Decreasing the

proportion of materials such as feldspar tends to decrease the enamel expansivity thus increasing the thermal-shock resistance. Increasing the proportion of materials such as flint produces the same effect (21).

Control of the bubble structure may eliminate freeze-thaw spalls. Firing may be extended to reduce the size and number of bubbles and, hence, reduce spalling (221). An excessive number of bubbles may also be prevented by proper choice of clays. (See also Crazing and Fracture.)

Thin Cover Coat

(See Bare Spots.)

Underfire

The appearance of an underfired coat is determined by the characteristics of the enamel. Clawson (82) describes an underfired cover coat as having a dull finish, rough to the touch. The defect is described also as incomplete fusion resulting in a dull and possibly exaggerated orange-peel surface (68).

Firing for too short a time or at too low a temperature produces underfired enamel. An underfired enamel can be corrected by immediate return to the furnace (82) and can be prevented by increasing firing time. (See also Roughness.)

Warpage

The terms "warpage" and "sag" both mean that the metal of the enameled article has become deformed during the firing operation (107), resulting in bowed surfaces (68). This is a defect of the steel. For example, sheets sometimes appear flat before enameling but buckle during firing (234).

Excessive refirings will promote warpage or sagging of the metal (228). As a general rule, higher firing temperatures, improper support of ware, and

the use of the thinner gauges of metal tend to cause warpage (190). Another cause may be strains left in the ware after shaping operations (190). The most important factors in understanding cause and cure of warpage are the relations of the firing temperature and the chemical compositions of the metal to the different transformations. In general, the amount of warpage increases as the carbon content increases. If the temperature of the transformation from the ferrite-austenite mixture to the wholly austenite structure is reached during firing, there is a large increase in warpage because of the relatively large volume change. In complicated shapes, this change does not occur simultaneously throughout, and serious warpage results. The temperature of transformation wholly into austenite decreases considerably with a slight increase in carbon content. Metalloids, such as manganese, act like carbon in decreasing this transformation temperature and are, therefore, added to the carbon content in estimating the temperature from the iron-carbon phase diagram. It is known that titanium in steel combines with carbon to form titanium carbide which is not soluble in iron. If sufficient titanium is present in enameling iron so that all the carbon is combined with the titanium, the iron has excellent sag and warpage resistance (107).

Waterlining

Waterlining consists of lines or depressions where movement of water in the unfired enamel has produced a concentration of salts and color (68). A high relative humidity, which retards evaporation of free moisture, is often responsible for waterlining. Humidity control and good air circulation often eliminate this defect.

Finely ground enamels, which require relatively large amounts of water in suspension per pound of dry enamel, have a greater tendency to waterline than do those that are coarsely ground.

Waterstreaks

(See Waterlining.)

Weld Blisters

Weld blisters are blisters in the enamel coating directly over a weldment.

The blistering of enamel over welded seams is caused by the evolution of hydrogen from the weld. Atomic hydrogen, present in most welding processes, is extremely soluble in molten weld metal. For this reason, large quantities of hydrogen are likely to be retained in the weldment (377).

Most of the hydrogen may be removed by peening and annealing the welded metal prior to enamel firing (267, 377, 61). Sandblasting the blistered surface free of enamel and re-enameling is necessary in some cases. (See also Blistering.)

Wrinkles

Wrinkles are microscopic waves in the enamel surface, which make the fired surface appear dull, silk, or matte. Wrinkling may be caused during cooling, when the outer layer becomes solid first, and then tries to follow the contraction as the inner layer cools and solidifies. Another common cause is the separation of crystals from supersaturated enamels.

When two different enamel coatings with different expansion coefficients are used together, wrinkling is particularly pronounced. If the melting points of the two are very different, they will try to react partially with each other. The reaction is not completed, because the firing process is too short.

This defect may be remedied by choosing enamels with equal melting points and by selecting the firing temperature in the critical range to relieve the tension between the outer and the inner layers during cooling (25). (See also Roughness.)

V. SUMMARY

Of the enamel defects discussed in this survey, the majority give rise to rejection of the enameled piece immediately after firing. In many cases, the source of the defect may be located and preventive measures taken during the process to eliminate further occurrence of the defect. Preventive measures may include such steps as addition of certain raw materials to the mill, modifying the grinding and slip preparation, correcting faulty application techniques, decreasing or increasing the drying or firing time, or changing the cooling time.

On the other hand, certain defects, particularly fish scaling, are of a delayed nature and may occur at any time after firing, possibly months later. It is difficult to predict and cope with such enamel defects.

Hydrogen gas has been found to cause either directly or indirectly many enamel defects. Many defect mechanisms associated with enameling are explained by hydrogen action. In particular, hydrogen is known to cause fish scaling. The gas accumulates beneath the hardened enamel coating and eventually builds up a greater pressure at the enamel metal interface than the enamel can withstand. At such a time (possibly months after firing), enamel failure occurs.

The sources of hydrogen are many. Pickling, cathodic electrolysis, rusting, welding, etc. produce hydrogen which may be absorbed by the base metal before it is enameled. During enamel firing, additional hydrogen is formed as a result of dissociation of water remaining in the bisque coat. Water in the bisque may react with the coated iron at firing temperatures to produce hydrogen. The hydrogen may also result from galvanic action on water in a molten cobalt-bearing enamel. The water dissolved in the frit apparently contributes in the greatest amount to the formation of hydrogen.

Moisture in the furnace atmosphere during the firing cycle possible tends to control the amount of water in the bisque and, thereby, is indirectly responsible for the production of hydrogen. Excessive moisture in the firing atmosphere tends to increase the hydrogen-caused defects.

Hydrogen in the dissociated or atomic state will enter into and diffuse throughout the base metal. Molecular hydrogen, on the other hand, is practically nondiffusible. However, above some elevated temperature, generally considered to be 800° C, molecular hydrogen dissociates to atomic hydrogen. The atomic gas diffuses into or effuses from the base metal. Below the dissociation temperature, if diffusing hydrogen encounters discontinuities in the metal structure, it will combine to form molecular hydrogen and the nondiffusible molecules become trapped and retained in the voids.

Hydrogen trapped as molecular hydrogen within the metal is not likely to cause enamel defects unless the enameled piece is refired at or above the dissociation temperature. Cold working the metal provides a network of discontinuities capable of occluding the gas, and it also produces laminations within the structure which impede the effusion of hydrogen normal to the plane surface. For this reason, cold-worked enameling metal tends to be relatively resistant to fish scale and similar defects. Shot peening is a cold-working process that has been recommended as a preventive measure for fish scaling. This process produces a surface layer consisting of deformed crystals and grains which prevents effusion of hydrogen. The thickness of the deformed layer is such that it is not effected by the pickling operation as sandblasted surfaces sometimes are.

If the enameled piece is reheated or refired, trapped hydrogen may become diffusible and possibly escape from the metal. When the temperature is high

enough for the coating to be molten, blister-type defects are likely to develop.

The thickness of the metal piece is related to the behavior of hydrogen and, therefore, to enamel defects. Thin sheet metal which can be easily freed of hydrogen seldom fish scale. Thicker sheet shows a corresponding increase in the tendency to produce fish scales. It is found, however, that thick plate metal is less likely to fish scale than thin plate. It appears that the thinner metal pieces are less affected by the hydrogen absorbed during firing. The hydrogen absorbed in the base metal is essentially constant for a given system independent of plate thickness. Upon cooling, the pressure of hydrogen which enters the metal during firing is a function of the confining volume of metal. Hence, thicker pieces are capable of retaining larger amounts of the gas without exhibiting defects.

A well-developed bubble structure in the enamel coating appears to prevent gas-formed defects. The bubbles provide space in which hydrogen collects. This action dissipates the pressure of hydrogen and possibly prevents the occurrence of defects.

It is obvious that the initial quantities of hydrogen should be reduced as much as possible. Hydrogen- and water-bearing enamel materials should be

kept to a minimum, and the amount of water retained or present in any source should be reduced as much as practical. Such action would greatly reduce the amount of gas-formed enamel defects.

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Engineering Experiment Station

VI. APPENDIX

General Bibliography of Enamel Defects

This bibliography contains references pertaining to enamel defects and defect-producing mechanisms.

The references which contain information concerning the enameling characteristics of steel plate are indicated by an asterisk. All references which have been reviewed for this report are indicated by double asterisks. All journals are referred to by the abbreviated form used in Chemical Abstracts.

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ENGINEERING EXPERIMENT STATION
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ANNUAL REPORT NO. 1

PROJECT NO. A-204

PORCELAIN ENAMELING QUALITY STEEL PLATES AND WELDMENTS

by

J. D. WALTON

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CONTRACT NO. NObs 66521
INDEX NO. NS-061-087
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I. ABSTRACT

The thermal shock test of MIL-P-16961B was passed with difficulty when the enamels suggested for the thermal shock test were used. However, an enamel was developed which contained 20 per cent aluminum oxide which not only passed all of the thermal shock requirements of MIL-P-16961B but an additional five quenches into cold water from a temperature of 1000° F.

The literature review required in SHIPS-P-1709 was completed September 1, 1955 and was titled, "Porcelain Enamel Defects Literature Review and Definitions."

Hydrogen studies were carried out whereby the hydrogen diffusion properties of steel could be determined as well as the amount of hydrogen injected into a steel sample during enameling. The latter test depended upon the hydrogen being extracted from the steel after enameling.

Hydrogen extraction data have shown that increased firing time, steel thickness and moisture in furnace atmosphere all increased the amount of hydrogen extracted from a given enameled steel specimen. Additional surface cold-working of the steel by shot-peening decreased the amount of hydrogen extracted.

No correlation appeared evident between the carbon content (or tendency to fish scale) of different steels and the amount of hydrogen extracted.

An adherence test was devised whereby adherence of enamel to steel plate and wledments could be determined. Other tests to determine oxidation characteristics and wetability are under development.

In order to better evaluate weldments, welding electrodes were studied from the standpoint of affinity for moisture of the electrode coating. These data will be correlated with the hydrogen injection tendency of the electrode during welding.

Correlation will be attempted between chemical composition, surface treatment of steel plates and weldments with hydrogen extraction, fish scale, adherence and wetability data.

II. PURPOSE

This project was initiated on January 15, 1955 and has as its objectives:

a. to determine the factors which affect the enameling characteristics of steel plates and weldments,

b. to establish the validity of parameters and set limits for control of quality necessary for enamelability of steel plates and weldments, and

c. to assess the factors responsible for defective coated parts intended to conform to Specification MIL-P-16961.

III. CONFERENCES AND VISITS

In order to meet the qualification requirements of MIL-P-16961B and to become familiar with the enameling properties of steel plates and weldments, conferences were held with representatives of the following companies:

A. O. Smith Corporation

Armco Steel Corporation

Atlantic Steel Company

Ferro Corporation

Inland Steel Company

International Nickel Laboratories

The Pfaudler Company

A visit was made to Seaporcel Metals, Inc., on July 21, 1955, to observe the coating of T-joint specimens with their M-16 enamel.

IV. EXPERIMENTAL WORK

A. Introduction

In order to carry out the objectives of Contract NObs-66521, the following line of experimental work was undertaken.

Ground-coat frits were secured which were reported to have satisfactorily passed the thermal-shock test of MIL-P-16961B. Steel strips and flats of thicknesses required for the T-joint specimens were secured and T-joints fabricated and coated.

In order to study some of the manifestations of hydrogen in steel, suitable pieces of apparatus were constructed. These consited of hydrogen diffusion and extraction equipment.

A program was also undertaken to study the effect of steel thickness, chemical composition and surface treatment as related to enamel adherence, tendency to fish scale and condition of enamel-metal interface. Concurrently with this, work was being undertaken to relate such welding variables as electrode composition, arc transfer efficiency and moisture pickup of electrode coating with injection of hydrogen into the welded steel, occurrence of fish scale and adherence.

Other studies which are in the formulation stages are oxidation characteristics of the steels, wetability of the steel in the presence and absence of oxygen as related to steel composition and surface treatment.

B. T-Joint Thermal-Shock Test

In order to pass the thermal-shock test of MIL-P-16961B, the following work was done.

1. Steels Used.

Since the Atlantic Steel Company had agreed to supply us with steels of varying compositions, this source of material was drawn upon for essentially all of the steel used in this initial work. By using strips and flats of a 4-inch width, the T-joint could be produced from one 8-inch length of strip 3/16-inch thick and one 4-inch length of flat 5/8-inch thick. The carbon content of the strips and flats was arbitrarily set at 0.12 per cent. One sample of 3/16-inch hot rolled steel plate with a carbon content of 0.03 per cent was secured from Atlantic Steel warehouse stock.

2. Welding Techniques.

The component pieces of the T-joint were assembled as shown in Figure 1 and welded by the manual-arc method using a Miller AC welder at a voltage setting of 200 V. The welding electrode used was General Electric's low-hydrogen electrode W-616A (AWS 6016) 5/32-inch D. Welding was first attempted using direct current, both normal and reversed, but excessive sputtering and blow-back resulted. This tendency was reduced somewhat by using alternating current.

3. Cleaning

Initially, the cleaning procedure used after fabrication consisted of sandblasting then burning at 1500° F for 30 minutes followed by a second sandblasting. As an added step, pickling followed as a means of reducing fish scaling when this defect was prevalent after the process described above was used.

4. Enamels Used and Developed

The ground-coat and cover-coat frits selected for use were recommended specifically for the thermal-shock test and were applied by spraying after the T-joints had been cleaned. Three ground-coat enamels were used and all exhibited some degree of fish scale.

An attempt was made to secure other ground-coat enamels, premilled and known to have satisfactorily passed the thermal-shock test. However, these enamels were not made available to us.

In an effort to overcome the fish scaling problem, it was decided that an attempt would be made to develop a ground-coat enamel which would not fish scale and at the same time would exhibit satisfactory thermal-shock resistance.

As a starting point, a ground-coat blend which matured at 1400° F was chosen. To this blend A-1 aluminum oxide was added in increments of 5 per cent. Each addition required a 50° F increase in maturing temperature to maintain a constant degree of adherence. With an alumina content of 20 per cent and a firing temperature of 1600° F, amazing mechanical flexibility of coating was obtained when the enameled piece was impacted to determine adherence. It was assumed that this flexibility should also indicate improved thermal-shock resistance.

During the development of this coating, it was necessary to obtain a new supply of A-1 alumina. This new alumina did not produce the same degree of elasticity as that originally used. Examination revealed that this difference was probably caused by a difference in particle size, the new alumina being coarser than the original. Since the original alumina was added to the slip after milling, it was found that this new alumina could be added to the mill during milling. Under these conditions, the resulting enamel had the same properties as the enamel which contained the original alumina added after milling. This brought up the interesting variable of aluminum oxide particle size which has not been given sufficient study. This variable will be given proper attention when studies are begun on mill additions at some future date.

5. Firing Techniques

a. Shrouding. It was anticipated at the beginning of this program that some difficulties would probably be encountered in equalizing the firing time between the 3/16- and 5/8-inch thick sections. Therefore, a means of shrouding the 3/16-inch section was devised (see Figure 2). The shroud was fabricated by welding two pieces of 4- by 3- by 5/8-inch plate together by means of two 1/4- by 1/2-inch pieces of strip iron to form a 4- by 8-inch rectangular section with an open area 4- by 2-inches in the center. This opening was designed to be located behind the area of juncture of the web and flange sections of the T-joint specimen, since the heating of this web area is slow enough that it requires no shrouding. In order to keep the shroud from touching the web section during firing, four screws were placed in the four corners of the shroud and extended through the shroud approximately 1/4-inch. The ends of the screws were ground to form small pins which served to separate the body of the shroud from the web. All firing was initially done using this technique. However, when the enamel was underfired, it could be seen that the shroud did not completely equalize the firing between the web and flange sections. Figure 3 shows the effect of thermal shocking such an underfired specimen. This specimen was quenched in cold water from a temperature of 800° F.

b. Firing Chamber. A firing chamber was constructed in order to eliminate the pin marks left on the back of the 3/16-inch section when fired with the shroud and at the same time provide a means of controlling the atmosphere surrounding the piece being fired. This chamber was fabricated from 12-gauge inconel and made in two sections resembling a rectangular box and lid (see Figure 4). By placing the T-joint specimens in the furnace, remarkably uniform heating and cooling of the entire T-joint was obtained.

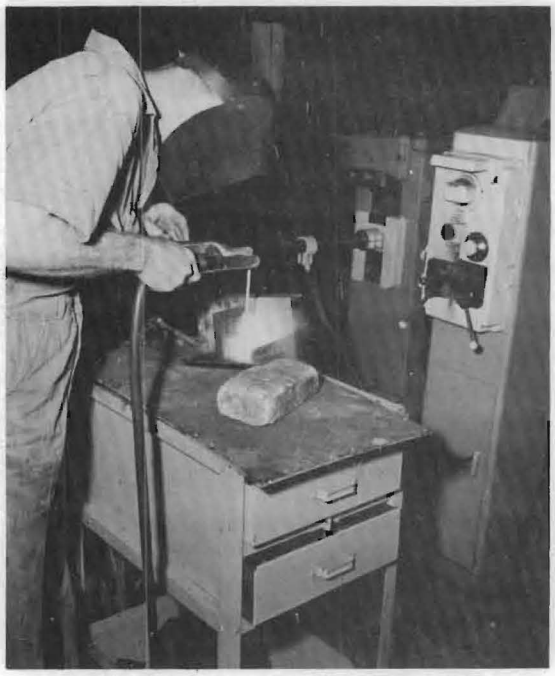

Figure 1. Welding of T-Joint in Assembly Holder.

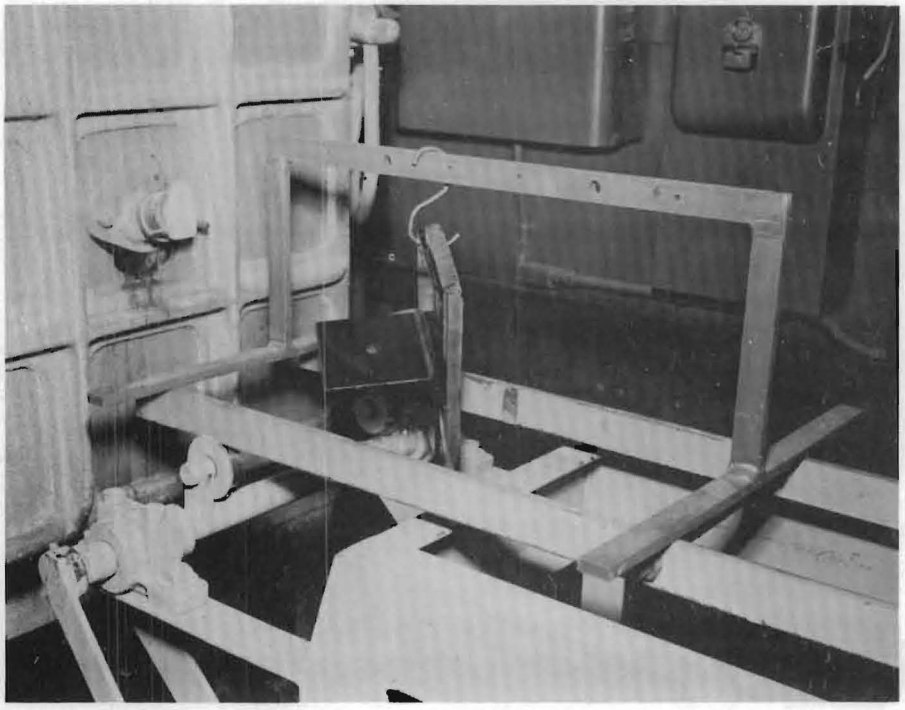

Figure 2. Firing Position of T-Joint with Shroud.

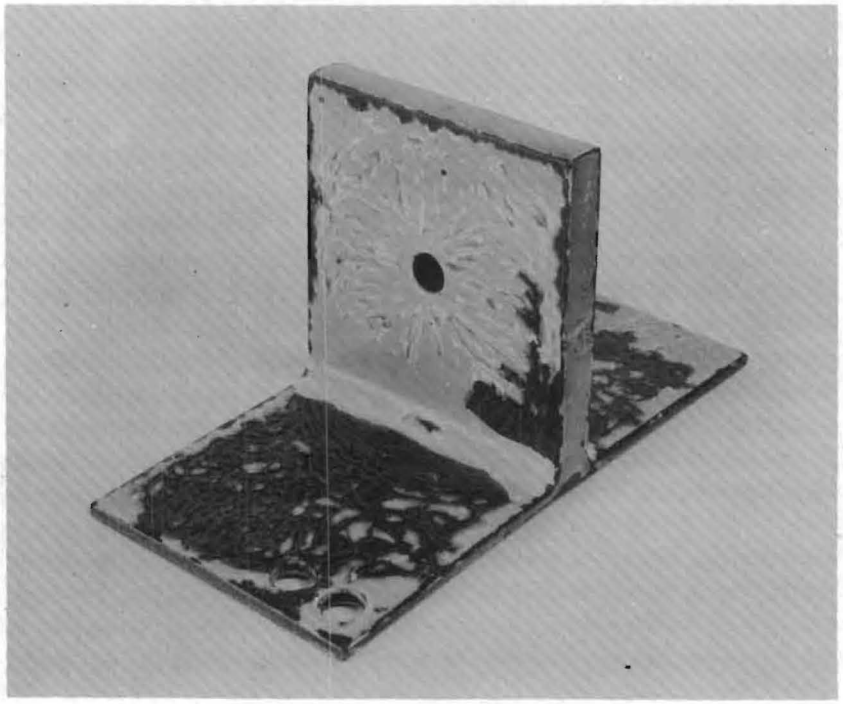

Figure 3. Underfired T-Joint after Thermal Shock.

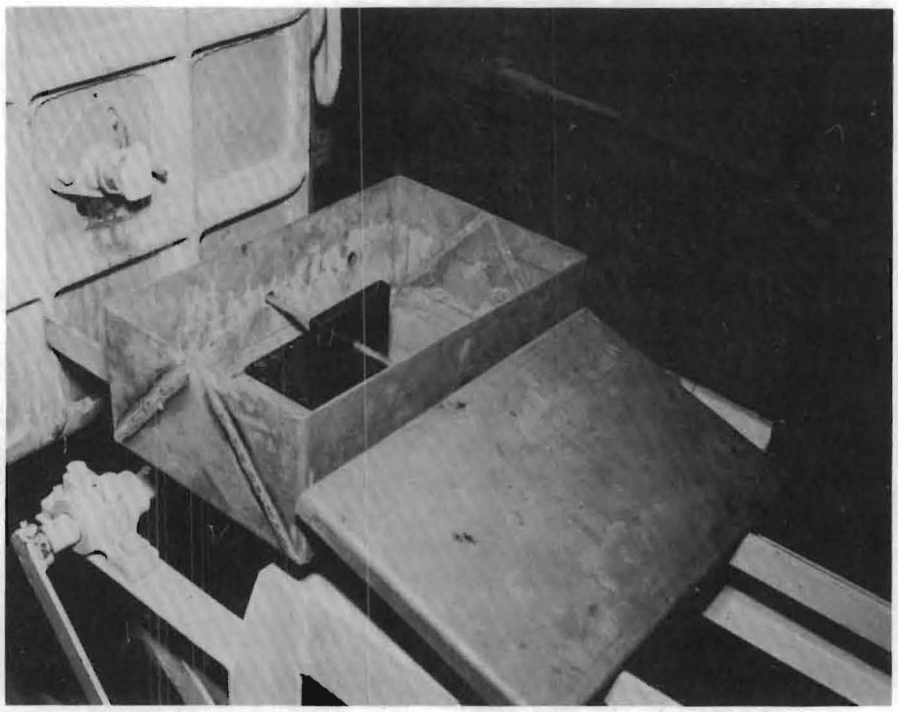

Figure 4. T-Joint in Firing Chamber.

c. Coating Evaluation. In order to evaluate coatings under the severest of firing conditions, the coated T-joint specimen was hung as shown in Figure 2 without the shroud shown in that figure.

The enamel which was described in chapter IV, B, 4, containing 20 per cent aluminum oxide, fired satisfactorily regardless of the technique used. This was the only enamel which could be fired without either the shroud or firing chamber and show neither underfiring of the flange section nor overfiring of the web section.

6. Thermal Shocking

Throughout this phase of the program, none of the enamels recommended for use as thermal-shock-resistant coatings passed the required thermal-shock schedule of MIL-P-16961B when C-1012 steel was used. However, when 0.03 per cent carbon steel was used for the web section, satisfactory results were obtained when the shroud was used in firing.

Fish scaling of the 3/16-inch web section was likewise prevalent in all cases where C-1012 steel was used. This, however, could be controlled to a certain extent by the cleaning technique employed. The best procedure for reducing fish scale was to sandblast, following with two minutes immersion in 6 per cent H_2SO_4 pickle solution at a temperature of 140°-160° F, then rinse, followed by five minutes in a single nickel-salt solution of 2 oz/gal at 140°-160° F and five minutes in a 0.1 per cent Na_2O neutralizer solution of sodium cyanide and meta silicate at 160°-180° F. Even though it was now possible to enamel the higher carbon web section without fish scale, these T-joints would not pass more than the five quenches from 800° F.

The enamel which was developed in chapter IV, B, 4, however, never exhibited fish scaling under any conditions of firing and at the same time passed all of

the phases of thermal shocking specified in MIL-P-16961B plus an additional five quenches in cold water from a temperature of 1000° F.

In order to better compare the recommended ground coats with the one developed, and at the same time evaluate the cover coat recommended for both acid resistance and thremal-shock resistance, the following experiment was carried out:

One-half of each side of a 4- by 8- by 3/16-inch strip of AISI C-1012 steel was coated with one of the recommended ground-coat enamels and the other half of each side coated with the ground-coat enamel developed. After firing, the entire specimen was coated with the desired cover-coat enamel and fired. This 4- by 8- by 3/16-inch section was subjected to all of the thermal shocking cycles specified in MIL-P-16961B plus an additional five quenches in cold water from 1000° F. This treatment completely removed the ground coat and cover coat from the half of the plate coated with the recommended ground coat. However, the half coated with the ground coat developed in chapter IV, B, 4 was completely intact with the exception of sharp corners and edges. The only evidence of thermal shocking was the presence of crazing in the cover-coat enamel.

In order to have comparative T-joint specimens for evaluating the coating applied in this laboratory, four T-joint samples were fabricated from AISI C-1012 steel for coating by Seaporcel Metals, Inc. with their M-16 enamel. The coating was witnessed by a Bureau of Ships representative on July 21, 1955.

Two of the samples were sandblasted at Georgia Tech, whereas the other pair were sandblasted at Seaporcel Metals. One of each pair was given a single coat of the proven ground coat and the remaining samples were given two coats of the same ground coat. These T-joint specimens were fired without benefit of shrouding and exhibited no evident detrimental effects from this severe firing treatment. The two specimens which were sandblasted at Seaporcel were thermal

shocked according to the schedule required in MIL-P-16961B. The single coated sample satisfactorily passed all quenches. However, the specimen with two coats failed after the third quench at 900° F.

C. Apparatus for Studying Hydrogen in Steel

Since fish scale is the most difficult defect to cope with in the enameling of steel plate, and this is a hydrogen defect (3, 5, 7, 8, 9, 10), it was decided that equipment would be constructed to study hydrogen in steel.

1. Hydrogen Diffusion

The apparatus shown in Figure 5 was constructed for the purpose of diffusing hydrogen through steel. The diffusion cell is shown in the middle of the figure suspended just above the surface of the water in the constant temperature bath. The cell is divided into two compartments separated by the steel sample undergoing investigation. The left portion of the cell contains the electrolyte which is an 11 per cent solution of H_2SO_4 with 0.05 g. of As_2O_3/1. of solution. The sample plate acts as the cathode with a platinum anode extending into the opening of the electrolyte cell. The right portion of the cell contains butyl phthlate and is fitted with a gas burette and leveling bulb. A direct current generator is used to supply a potential between the platinum anode and steel sample cathode which causes direct current to flow through the electrolyte. The body of the cell is kept at a constant temperature of 35° C through immersion in the water bath. This apparatus is similar to that used by Bryant et al. (2).

Hydrogen is formed at the face of the steel plate in contact with the electrolyte. Some atomic hydrogen, however, remains in the steel and passes through

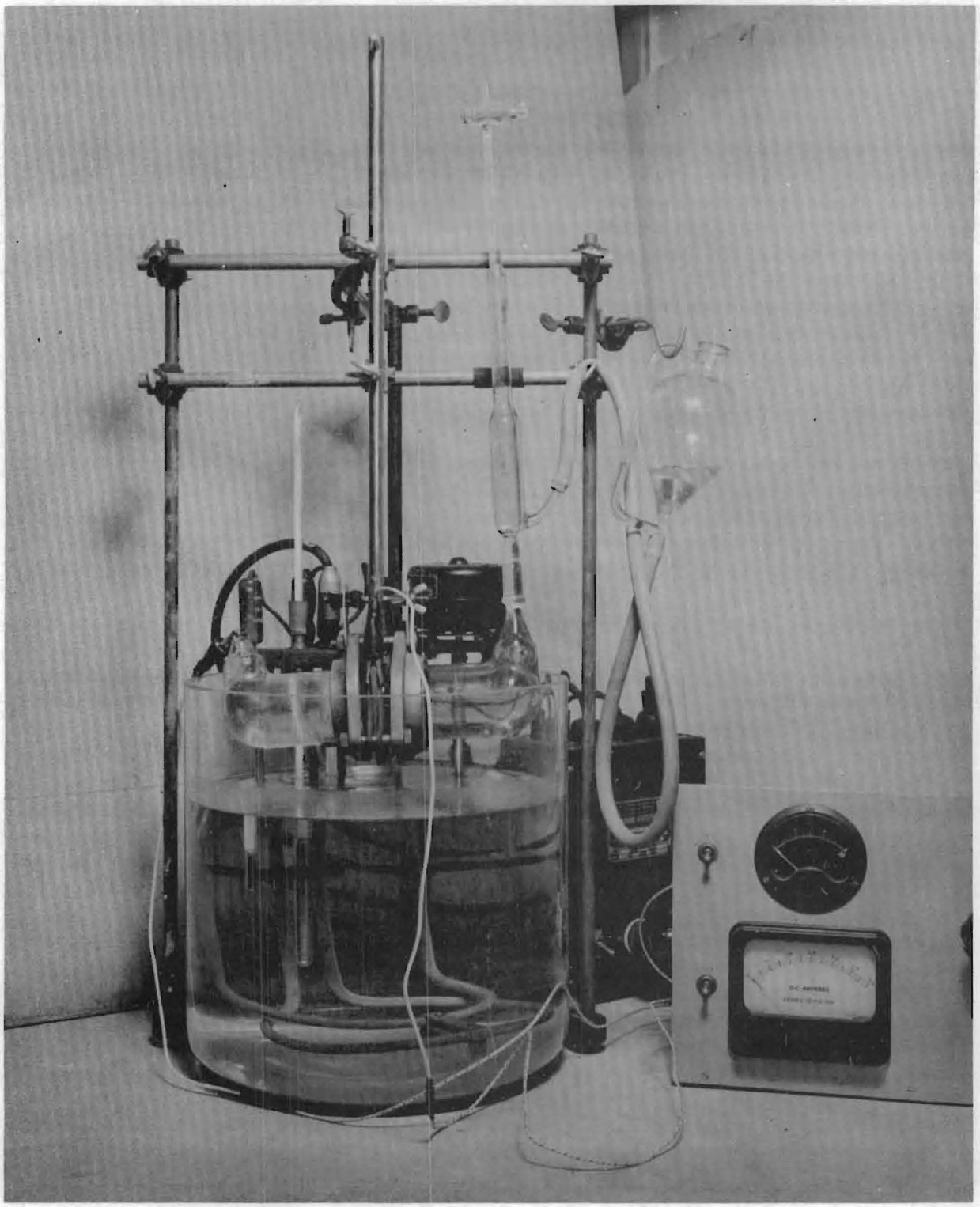

Figure 5. Hydrogen Diffusion Apparatus.

to form molecular or gaseous hydrogen in the butyl phthalate and is collected in the gas burette and measured under atmospheric conditions of temperature and pressure. This collected hydrogen is referred to as diffused hydrogen.

Since the reference (2) in the literature delt with the diffusion of hydrogen through sheet steel, it was decided that first attempts to carry out such work would be done by using 18-gauge enameling iron.

Reproduceability between samples was found to be very poor unless comparable samples were cut adjacent to one another. All samples used were 3- by 4-inches. However, the area in contact with the electrolyte was π square inches, as determined by the 2-inch diameter of the cell opening. Two samples, A and Z, cut from opposite ends of a two-foot strip whose length paralleled the direction of rolling, were set up in the diffusion apparatus. The average rate of diffusion of A was 0.02 ml/min in 100 minutes while Z was 0.03 ml/min over the same period. Sample B was then cut adjacent to A and Y next to Z. The average rate of diffusion for B was 0.023 ml/min and Z was 0.033 ml/min. This reproduceability was possible only when cleaning with a wire wheel was employed. A much greater discrepancy was observed when sandblasting was used as the method of cleaning. All of these tests were carried out at a potential of 3.5 volts with 1 amp of current flowing. Lower voltage appeared to improve reproduceability. However, at this point, it appeared that the effect of surface treatment should be studied and more attention given to diffusion studies using steel plate.

2. Hydrogen Extraction

Since the hydrogen injected into the steel by any of several mechanisms (6) appears to be the cause of fish scale, the apparatus shown in Figure 6

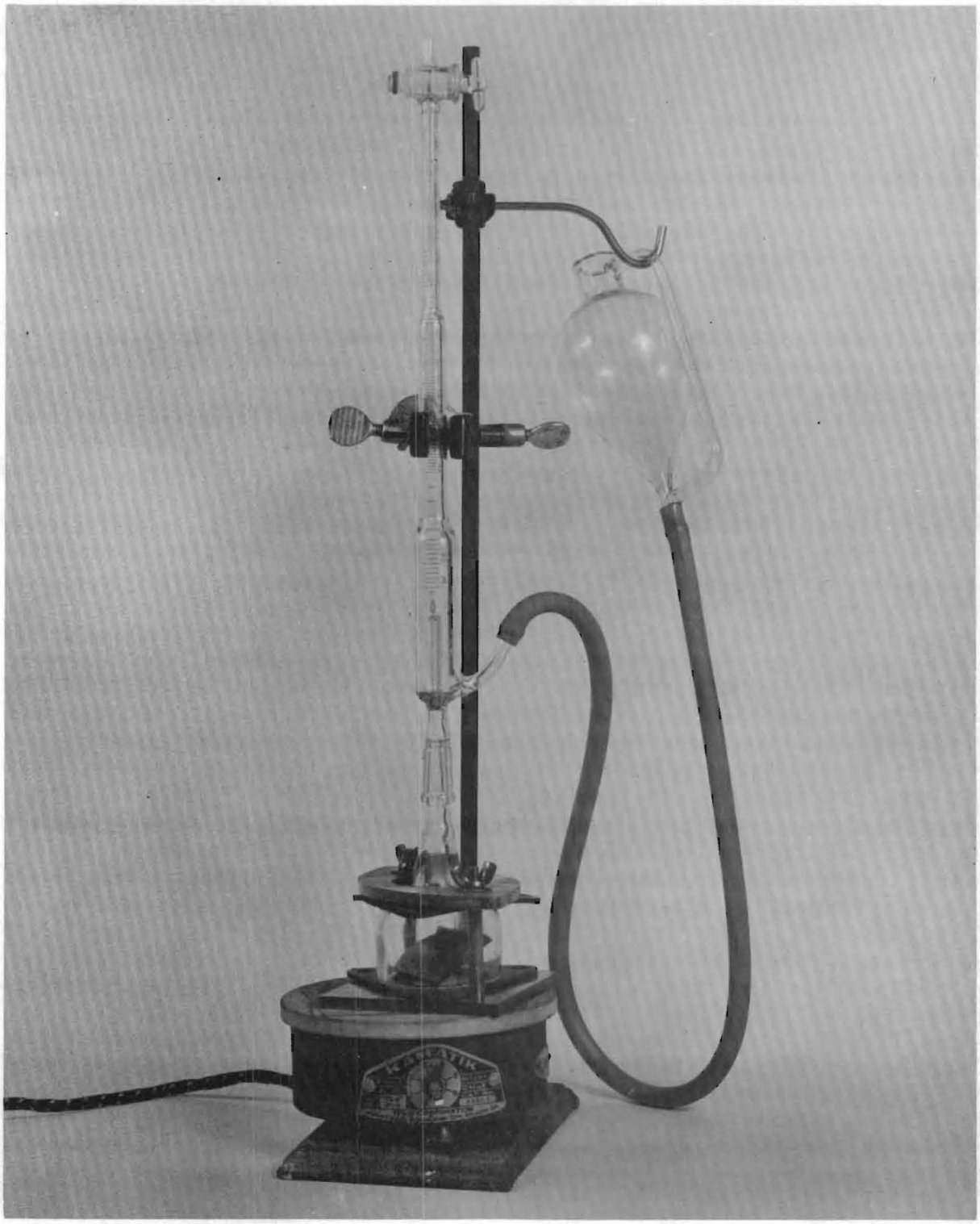

Figure 6. Hydrogen Extraction Apparatus.

was constructed with which hydrogen could be extracted from steel. Thus the various reported sources of hydrogen could be evaluated and their relative importance determined.

The extraction chamber consists of a bell jar fitted with a standard taper joint. This jar is clamped to a stainless steel plate and a seal is effected by means of an asbestos gasket. A gas burette with leveling bulb is fitted to the top of the jar.

A 1-1/2- by 2-inch steel sample is placed in the jar and mercury added until the sample is submerged. Butyl phthalate is then added to cover the mercury and fill the gas burette. The system is then placed on a hot plate which is adjusted to maintain a mercury temperature of 170° C. The system is then left overnight and the hydrogen collected during this period is reported as extractable hydrogen.

A 1-1/2- by 2-inch piece of 3/16-inch plate, placed in the apparatus as previously described, liberated only one small bubble of gas overnight. This amounts to only a fraction of the first division on the burette which is 0.05 ml. The same amount was extracted when a similar piece was heated at 1560° F for 15 minutes and cleaned with a wire wheel. When the same steel was coated with the ground coat used for coating the T-joint specimens and heated in the extraction apparatus overnight, 0.14 ml of gas was liberated and the piece exhibited fish scale.

In order to investigate another of the causes of fish scale, a piece of the same steel was treated as above except that during the firing of the coating, air was passed through boiling water and injected into the furnace. This piece liberated 0.82 mls of gas and was severely fish scaled.

A study of the effect of a moist atmosphere on the uncoated steel when heated to firing temperatures was carried out next. Under the same condition as the previous test, but without a coating on the steel, it was found that, again, only a small bubble of gas was liberated. However, when a similar piece was put in the furnace, lying upon a wet refractory pallet with water continuously dropped on the surface of the specimen throughout the heating cycle, a total of 0.55 ml of gas was extracted.

The importance of acid pickling as a source of hydrogen was touched upon by immersing a test specimen in a 6 per cent H_2SO_4 solution at 175° F for a period of 10 minutes. The gas extracted after this treatment was 0.14 ml.

A piece of steel plate which had had hydrogen diffused through it in the hydrogen-diffusion apparatus was set up in the extraction apparatus. A volume of 1.54 ml of hydrogen was extracted. It might be assumed in this instance that the steel was saturated with hydrogen. Thus, in the case of the enameled piece fired in a moist atmosphere, more than 50 per cent saturation with hydrogen was obtained.

In this test, the hydrogen extracted from an enameled piece depended upon its being liberated from fish scales formed in the enameled piece. It was desirable, however, to determine the amount of hydrogen injected into a given steel whether the enamel fish scaled or not.

One other limitation was evident in this test. When considerable fish scaling was produced in a specimen, it was not possible to collect all of the hydrogen liberated. This resulted from the fact that as the specimen cooled through the range of 300° to 500° F, fish scaling commenced. In this temperature range, very little time is required for hydrogen to diffuse through and

out of steel, and yet the specimen was still too hot to be set up in the apparatus. In order to overcome the slow cooling of the sample and at the same time prevent the test from being dependent upon hydrogen being liberated only through the fish scaling of the enamel, the following procedure of sample preparation was developed.

The specimen was enameled in the desired atmosphere as in the previous test. However, upon being removed from the furnace, it was immediately plunged into ice water As soon as it was cool enough to handle, the specimen was sandblasted and set up in the extraction apparatus.

By this technique, the metal cooled rapidly through the temperature range in which hydrogen diffuses most readily through steel. By removing the coating, the hydrogen was free to leave the steel without the necessity for the coating to fish scale.

As a final development in this test, the apparatus was modified in the following manner. The bell-jar portion of the apparatus was constructed in two sections. The upper section was composed of a 1-inch Pyrex glass pipe nipple with the standard taper joint welded to one end. This was permanently secured to a 2- by 1-inch reducer by means of flanges designed for that purpose. A seal between the two joints was effected by means of a Teflon gasket. The 2- by 1-inch reducer was then secured to the stainless steel base plate and served to contain the steel specimen and mercury. A Teflon gasket likewise provided a vacuum-tight seal between the glass pipe and the stainless steel plate. Three stainless steel pins silver-soldered in the stainless steel plate served to hold the specimen in a vertical position (see Figure 7).

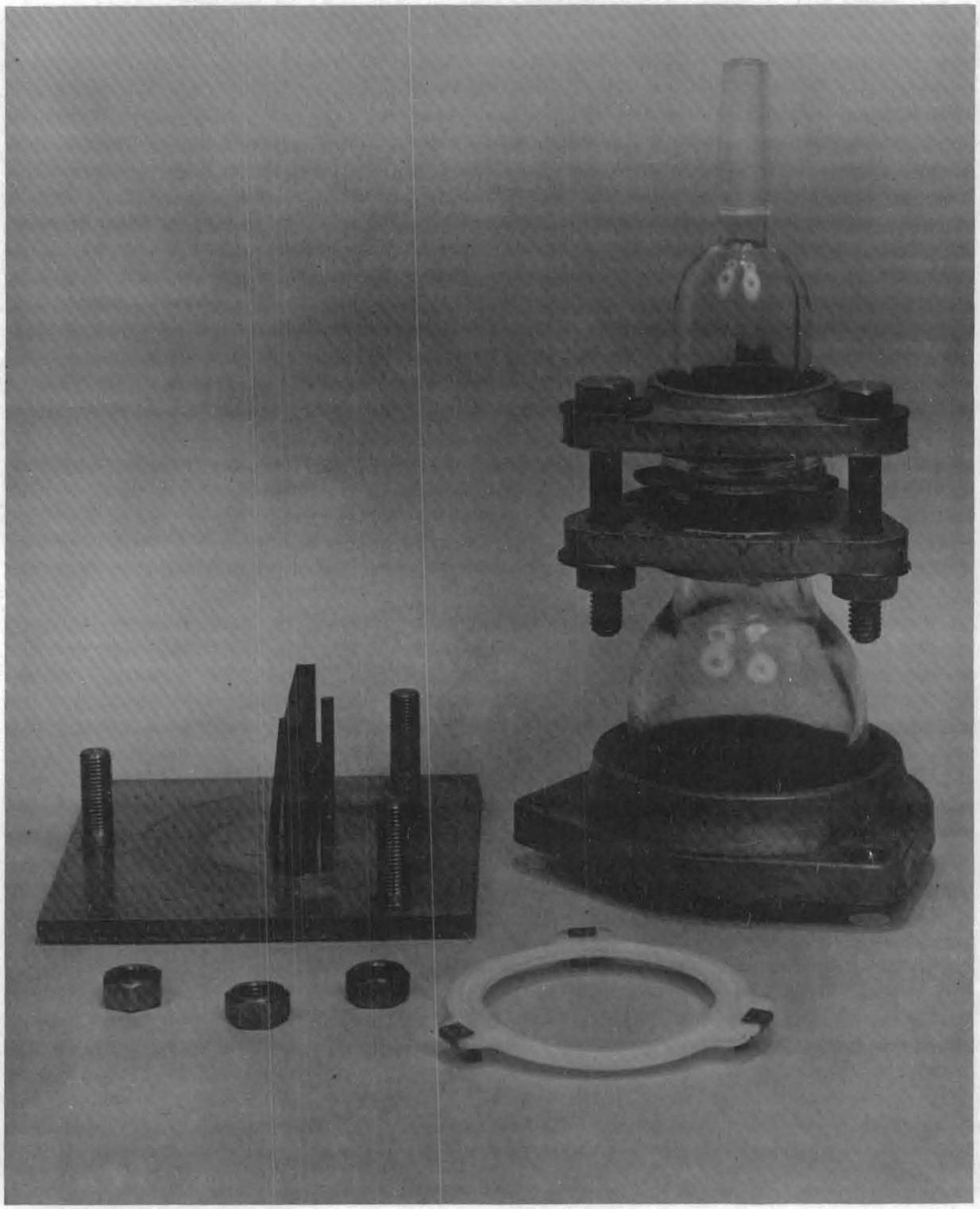

Figure 7. Modified Hydrogen Extraction Apparatus.

The following procedure was used in determining extractable hydrogen.

The enameled 2- by 1-1/2-inch specimen was quenched in ice water immediately upon removal from the furnace. As soon as the piece was as cool as the surrounding water, it was dried, sandblasted and set up in the extraction apparatus. Mercury was added to cover the specimen, and the system was evacuated in order to remove any entrapped gases. The gas burette was then placed on the standard taper joint, and the remainder of the system was filled with butyl phthalate. The apparatus was then placed on a hot plate and heated to 175° C.

All firing was done in a small muffle furnace. The moisture in the furnace atmosphere was controlled in the following manner. Compressed air was controlled by means of a reducer valve to a rate of flow of 200 cc/min as measured by a flow rater. The air was then bubbled through water which half filled a filter flask and then through a stainless steel tube inserted into an observation hole in the door of the furnace. The specimen was fired by passing air into the furnace for a period of 10 minutes, after which time the tube was removed from the furnace door, the specimen placed in the furnace and the tube reinserted into the furnace. Figure 8 shows the effect of firing time and the temperature of the water through which the air entering the furnace was passed on the amount of hydrogen extracted from the enameled piece.

D. Steel Variables Under Consideration

1. Chemical Composition

Samples of flats with carbon contents of 0.09, 0.15, 0.24 and 0.35 per cent were secured from the Atlantic Steel Company in order to determine the significance of this variable on the enamelability and thermal-shock resistance of the steel.

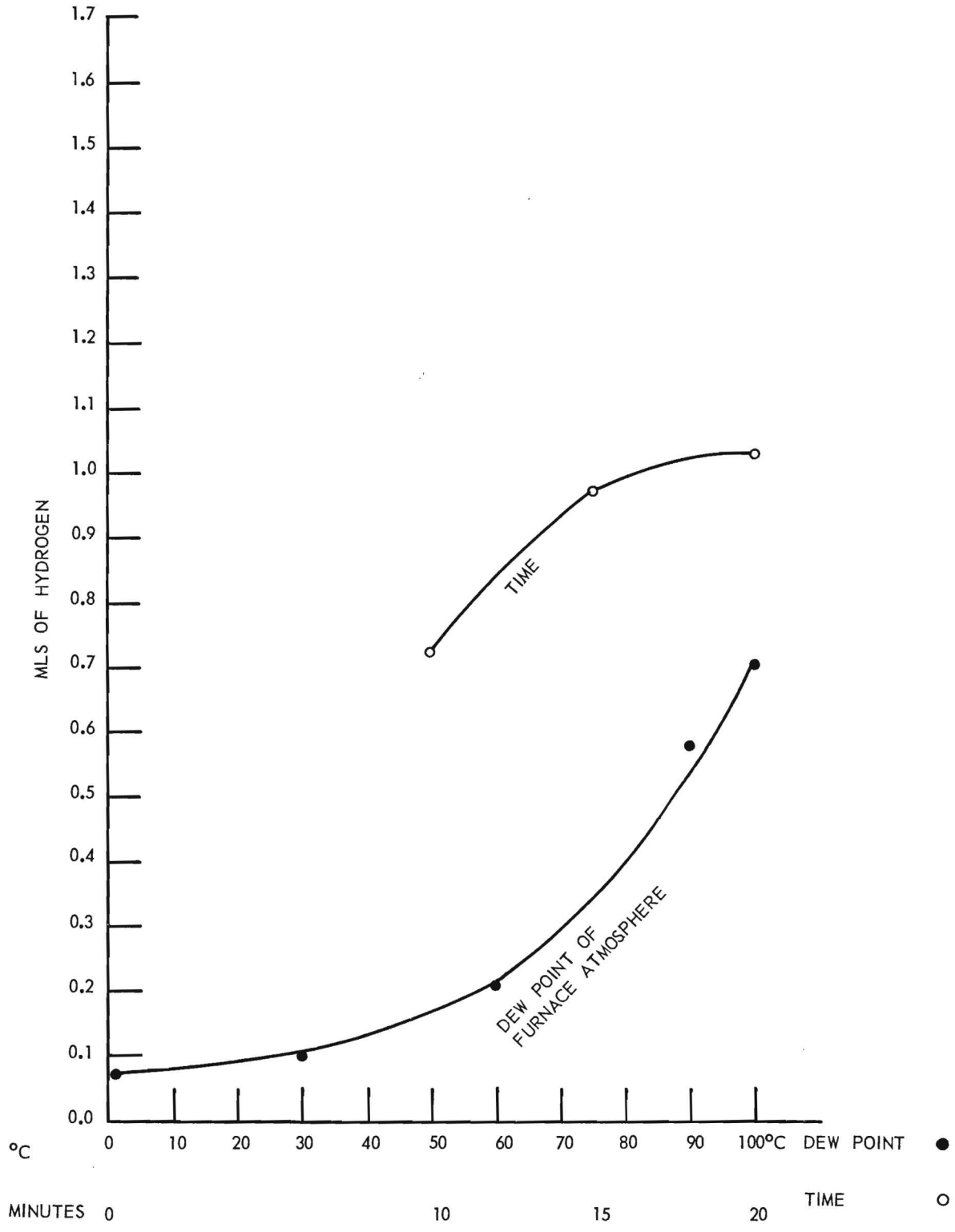

Figure 8. Effect of Firing Time and Amount of Moisture in Furnace Atmosphere on Amount of Hydrogen Extracted.

Two plates were made from these four pieces of steel flat. One plate was made by butt welding two pieces of 1/2- by 3- by 6-inch steel flat together to form a 1/2- by 6- by 6-inch plate. The carbon content of one of the component plates was 0.09 per cent and the other was 0.24 per cent. The second test plate was fabricated in a similar manner except the plate thickness was 3/8-inch and the carbon content of the component pieces was 0.15 and 0.35 per cent.

During the cooling of these plates, after firing, it was observed that the lower carbon content strip of each plate cooled noticeably more slowly than the higher carbon component. After ground coating and cover coating, these plates were subjected to three quenches in cold water from 800° F. The lower carbon component of each plate exhibited large areas of spalling ranging from 3/8-inch diameter spalls to 4- by 1-inch spalled sections. However, the 0.24 per cent carbon piece exhibited only nine fish scales located along the outer edge of the piece, and the 0.35 per cent carbon piece exhibited only one isolated fish scale.

The welded areas of these plates, as well as the T-joint specimens thus far fabricated, have been significantly free of defects.

Extractable hydrogen was determined for three different grades of AISI steel as well as for capped, rimmed and Lukens T-1 steel. These data are reported in Table I.

2. Surface Condition

a. Chemical Cleaning. The only chemical cleaning done other than that used in the case of the T-joint specimens, was accomplished by the use of

TABLE I

SUMMARY OF CHEMICAL, PHYSICAL AND HYDROGEN EXTRACTION DATA OF EIGHT STEELS USED

Type of Steel	Form	Thickness (in.)	Analysis C	Mn	P	S	Cu	Si	Cr	Ni	V	Mo	B	Gas (ml)	Fish Scale
C-1006	1-1/2-inch strip	1/8	.08	.34	.010	.036	.34	----	---	---	---	---	-----	0.67	Slight
C-1012	1-1/2-inch strip	1/8	.12	.44	.010	.034	.37	----	---	---	---	---	-----	0.59	Slight
C-1017	1-1/2-inch strip	1/8	.16	.43	.010	.028	.32	----	---	---	---	---	-----	0.71	Slight
C-1012	4-inch strip	3/16	.12	.48	.010	.010	.23	----	---	---	---	---	-----	0.70	Severe
Capped	Plate	3/16	.06	.36	.010	.026	---	.008	---	---	---	---	-----	0.79	Slight
Rimmed	H. R. Coil	0.17	.07	.38	.006	.025	.02	.007	.01	.02	---	---	-----	0.52	Very Slight
Rimmed	C. R. Coil	0.126	.07	.38	.006	.025	.02	.007	.01	.02	---	---	-----	0.74	None
Lukens T-1	Plate	1/4†	.15	.75	.026	.026	.36	.24	.50	.85	.05	.45	.0029	1.11	None

†Typical analysis

NOTE: All samples were sandblasted prior to enameling.

of sodium hydride. The effect of this type of cleaning on the amount of hydrogen extracted, before and after sandblasting, is shown in Figure 9.

b. Sandblasting. To evaluate the effect of sandblasting on the hydrogen diffusion properties of 18-gauge enameling iron, two samples were prepared by sandblasting. Sample 1 was sandblasted just enough to clean the surface, whereas sample 2 was sandblasted much more severely. As a result, 2.50 ml were diffused through sample 1 over a period of 150 minutes, while only 1.15 ml were diffused through sample 2 over the same period of time. A repeat of this experiment produced values of 1.55 for the normally sandblasted piece and 0.05 for the excessively sandblasted piece, both over a period of 150 minutes. Although the values from individual pieces, heavily sandblasted, varied to a considerable extent, it was still thought that a significant difference was observed as a result of sandblasting.

c. Shot-Peening. The effect of shot-peening on the injection of hydrogen into steel was determined by means of the hydrogen extraction apparatus. Figure 10 represents the data obtained from samples of 3/16-inch C-1012 steel receiving various degrees of shot-peening. The curve representing shot size was obtained from samples subjected to a constant shot-exposure time of 15 minutes and constant shot velocity resulting from a wheel speed of 2250 rpm with the shot size which varied from S-70-WSS to S-230-WSS. The shot-velocity curve was obtained from samples receiving the same exposure time as the previous test and the shot size held constant at S-170-WSS but with the velocity of the shot resulting from a wheel-speed variation from 1500 to 2470 rpm. The exposure-time curve represents the variable of time from 5 to 30 minutes with a wheel velocity of 2250 rpm and shot size of S-170-WSS held constant.

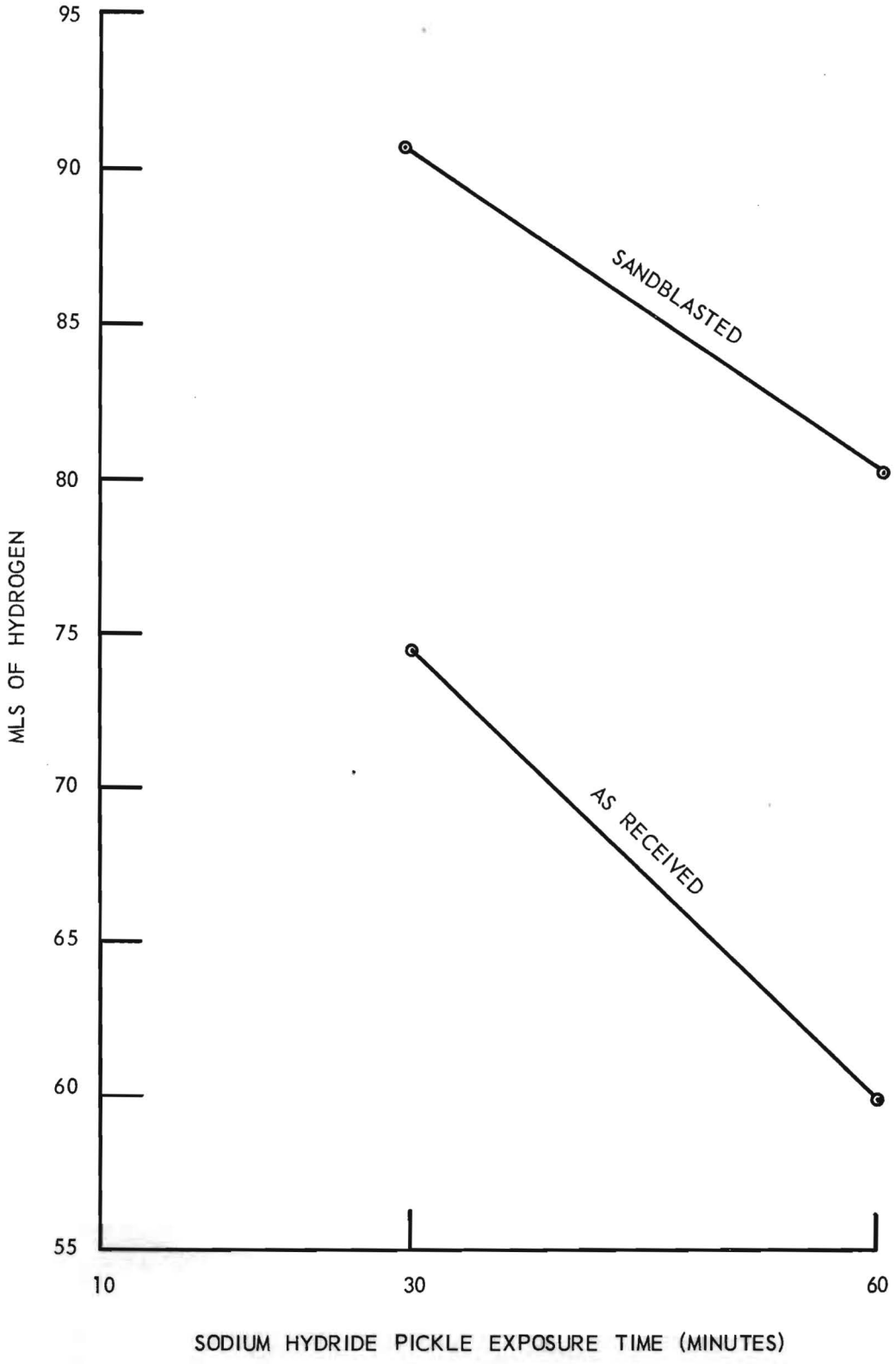

Figure 9. Effect of Sodium Hydride Pickle Time on Amount of Hydrogen Extracted.

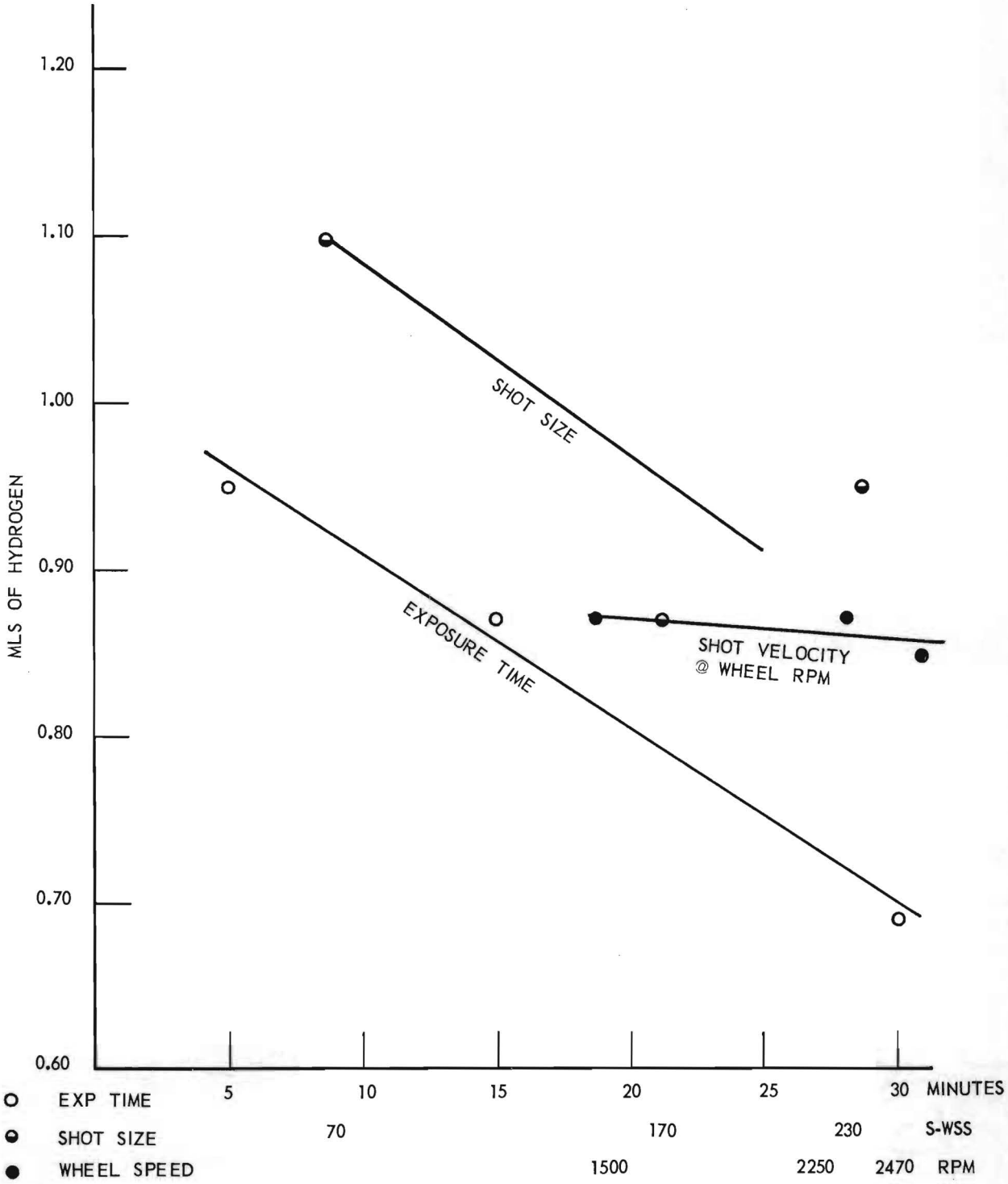

Figure 10. Effect of Shot-Penning on Amount of Hydrogen Extracted.

d. Hot and Cold Reduction. As a preliminary experiment to relate method of reduction with extractable hydrogen, a sample of rimmed steel was obtained in two stages of reduction. These specimens were enameled and the extracted hydrogen is reported in Table I.

3. Thickness

The effect of steel thickness on extractable hydrogen is shown in Figure 11. The curve A-B-C-F was obtained by machining four 1 1/2- by 2-inch specimens from 4- by 3-inch piece of 5/8 -inch C-1012 flat to the thicknesses shown. Point F represents the 5/8-inch-thick specimen without machining. The curve D-E-F was obtained by securing the C-1012 strip in the desired thickness.

E. Adherence

Adherence studies were begun using the stretch-test method of J. E. Sams, described in "Proceedings of the Fifth Annual Forum", Porcelain Enamel Institute, 1940. The sample size selected for use in this test was 2- by 14- by 3/16-inch. After sandblasting, the specimen was ground coated, by spraying, and then dried. Before firing, approximately two inches of enamel were brushed from each end and two 1/2-inch-wide strips separated by three inches, were brushed equidistant from the center of the strip. Thus, a three inch portion of the center of the strip was left undisturbed.

After firing, an extensiometer, which was constructed for this test, was attached to the specimen at the 1/2-inch-wide strips left unenameled. The entire assembly was then set up in a Riehle 6000 lb. Universal testing machine (see Figure 12).

Stretching of the piece was begun and was continued until the extensiometer indicated the desired per cent elongation of the 3-inch test area in the center

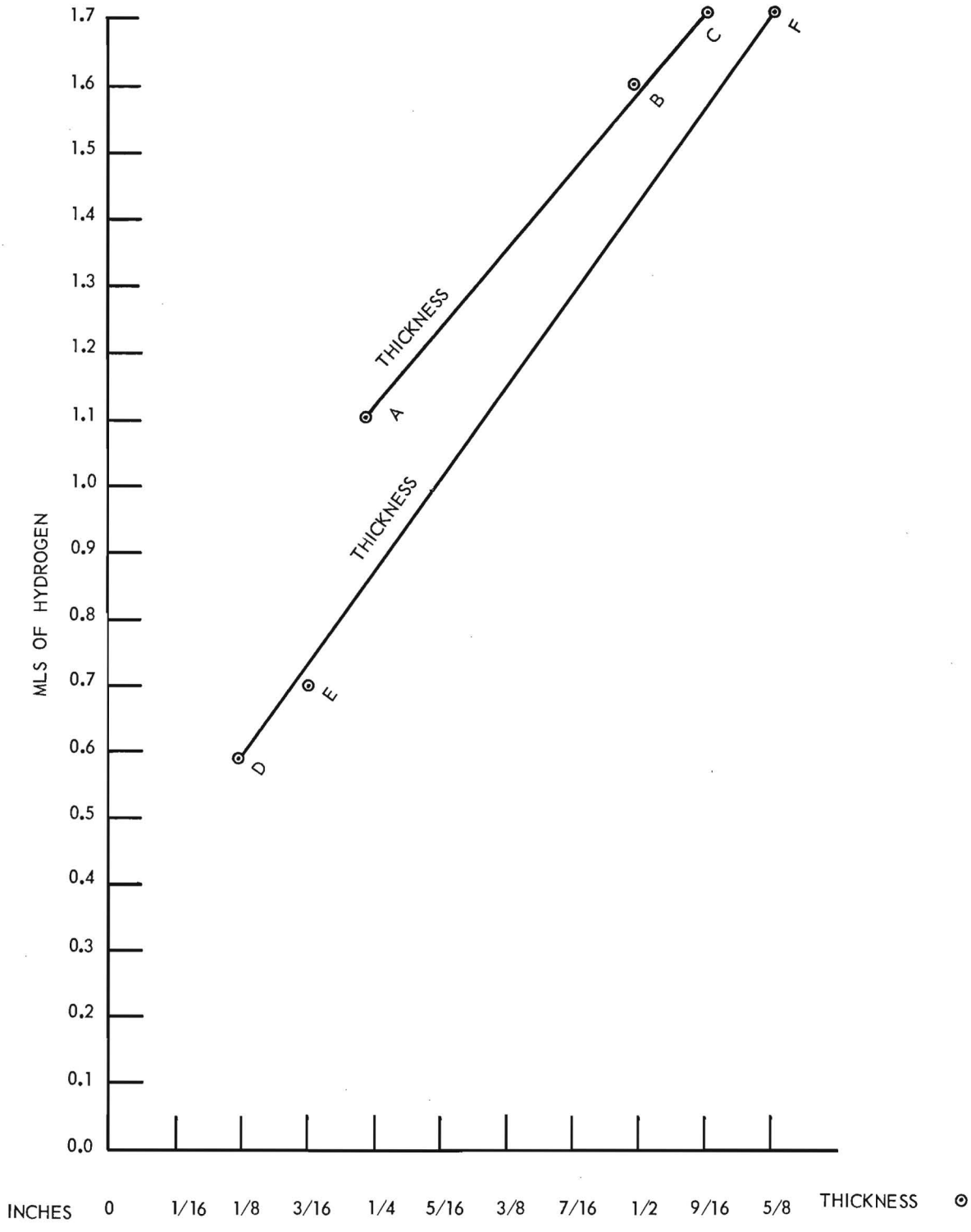

Figure 11. Effect of Metal Thickness on Amount of Hydrogen Extracted.

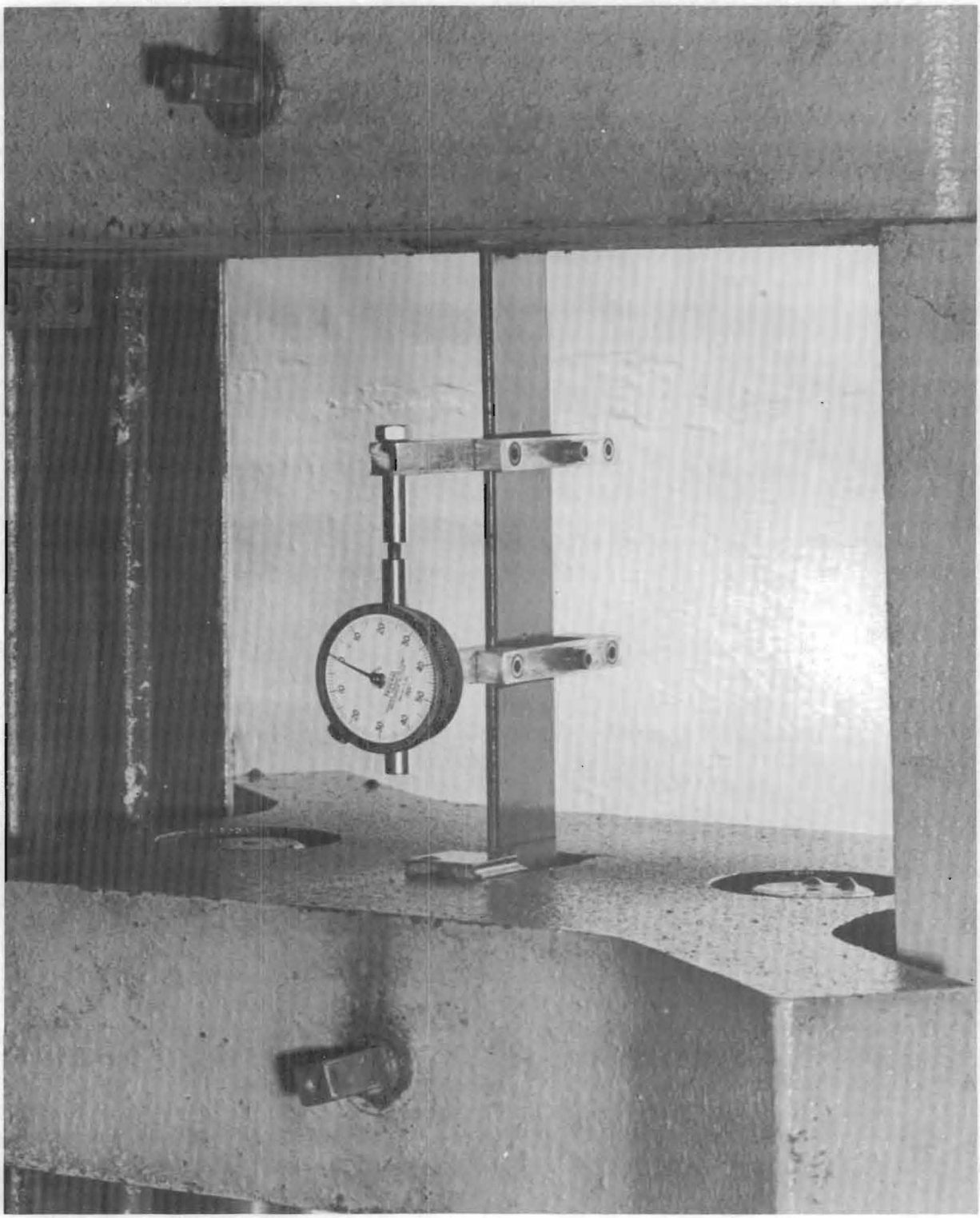

Figure 12. Set up for Stretch Testing Adherence of Enamel to Steel Plate.

of the specimen. Figure 13 shows the effect of 3 per cent and 6 per cent elongation. Table II presents the data obtained when adherence strips of AISI C-1010 steel were coated with one of the ground-coat enamels used in the T-joint thermal-shock tests. These specimens were fired at 1560° F for the periods of time shown. All were stretched 6 per cent prior to having the adherence counts determined.

TABLE II

EFFECT OF FIRING TIME ON ADHERENCE

Firing Time	Side	Thickness (mils)	Count	Average Thickness	Average Count
10	Front	3-4	451	3.5	450
	Back	3-4	448		
10	Front	3-4	380	3.5	370
	Back	3-4	360		
15	Front	4	357	3.5	344
	Back	3-4	331		
20	Front	4	275	4	308
	Back	---	341		

Count as determined by PEI Adherence Meter.

Optimum Adherence = 0 counts.

No adherence = 507 counts.

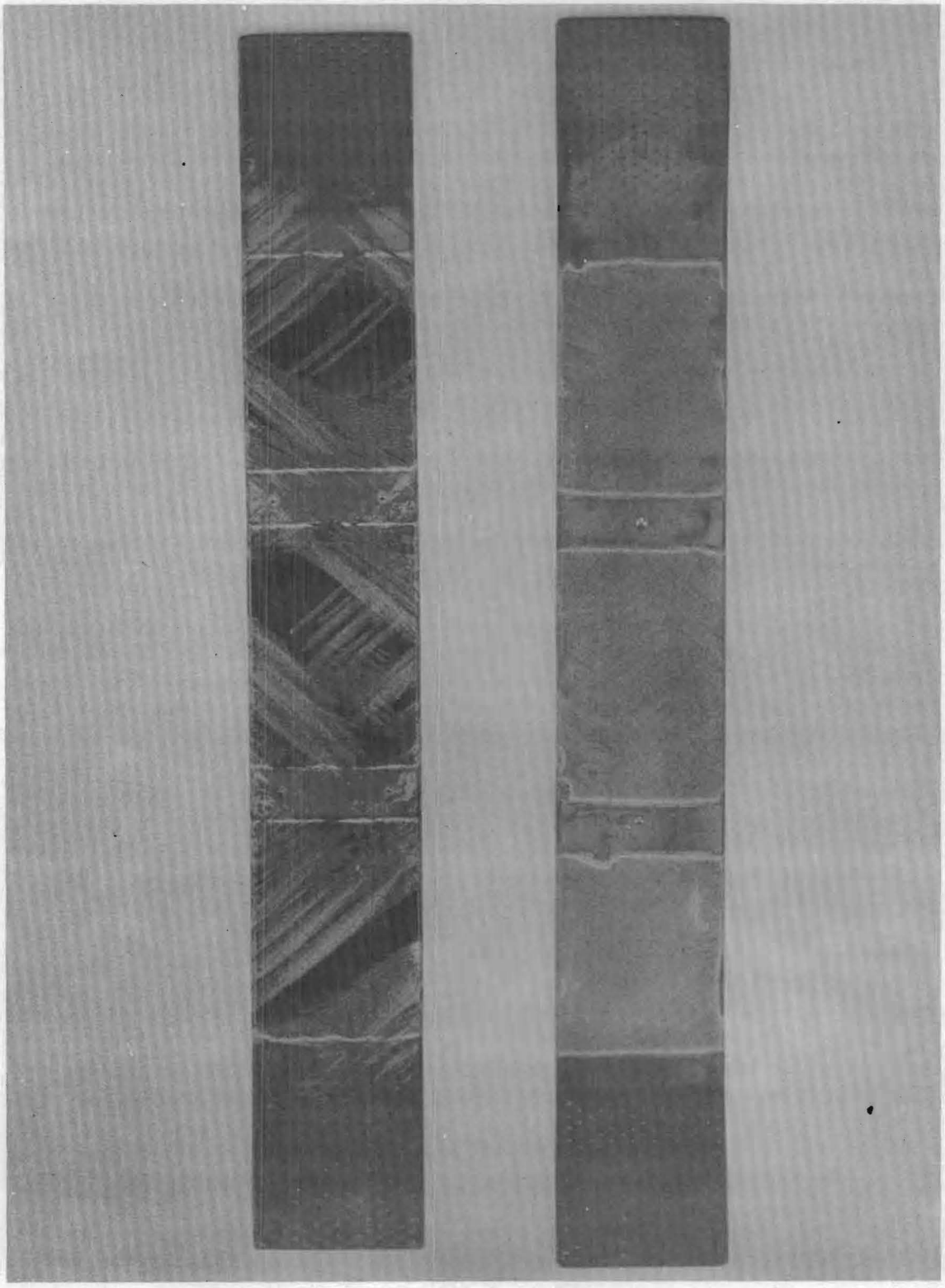

Figure 13. Effect of Per Cent Elongation of Adherence.

F. Welding

Welding studies have begun with the procurement of AWS specified welding electrodes for mild and low-alloy steels. Twelve such specifications represented by eight manufacturers have been received. Five electrodes are represented by at least six manufacturers, and five by less than three.

1. Electrode Coating

Since it appeared that one of the primary differences between given electrodes was the electrode coating, it was decided that tests would be developed for studying this part of the electrode separately. Hydrogen in steel is responsible for fish scale (3, 5, 7, 8, 9, 10) and water dissociates at arc-welding temperatures to form hydrogen. Therefore, the affinity for moisture of the electrode coating was the first variable to be studied.

In order to determine the rate of moisture pickup of the coating, the following test was devised. Two and one-half inch lengths of each electrode were cut, the coating removed and weight-per-unit length of the electrode metal was determined. Additional lengths of electrode were then cut and dried at a temperature of 180° C. These specimens were then allowed to cool to room temperature in a vacuum over a drying agent. After cooling, each specimen was weighed and the length of metal determined. From the previous data, the weight of electrode metal was determined and subtracted in order to obtain the weight of dried coating.

All specimens were next placed in a sealed chamber containing water, and left at room temperature. Each electrode was then weighed periodically in order to determine the rate of moisture pickup of each coating. These data were then tabulated and two electrodes of each AWS specification selected on the basis of

maximum and minimum moisture adsorption. Each manufacturer was also selected on the basis of being represented by at least two AWS specifications. These selected rods, manufacturers and moisture pickup data are represented in Table III.

2. Adherence

In order to study the adherence of enamel to welded areas, the following test was devised.

Two 1- by 14- by 3/16-inch lengths of AISI C-1014 steel were butt welded with the desired electrode to form a 2- by 14- by 3/16-inch strip with the welded area down the middle of the strip. This weld was ground flush with the base metal, sandblasted and treated as a specimen for the stretch test described in V.E.

G. Photomicrographs

Photomicrographs were made of several enamel-metal interfaces as well as the bubble structure of the enamels themselves This was done in an effort to become more familiar with the appearance of these systems.

Figures 14-18 show the enamel-metal interfaces of the recommended enamel on five different steels. These were the AISI C-1012 steel used in fabricating the T-joint specimens, capped steel, rimmed steel 0.17-inch thick, rimmed steel 0.126-inch thick (same as above after cold rolling) and T-1 steel.

Figures 19-20 show the bubble structure of the recommended enamel fired for 10 and 15 minutes. Figures 21-23 show the enamel used as the basis for developing the thermal-shock-resistant ground coat and the effect of the addition of 10 and 20 per cent aluminum oxide.

TABLE III

MOISTURE PICKUP OF ELECTRODE COATINGS IN 100 PER CENT RELATIVE HUMIDITY

Manufacturers	hrs	6010	6011	6012	6013	6016	6024	6027	7016	7020	10013	10016	No Class
Airco	4					0.49							
	24					5.89							
	120					7.15							
Gen. Elec.	4										0.47††	0.48	
	24										2.45	4.80	
	120										8.17	6.68	
Hobart	4		1.46	0.34	0.78		0.05	0.84	0.03				
	24		17.33	3.88	4.56		0.84	2.03	1.11				
	120		22.99	6.36	7.16		1.70	6.10	3.40				
Lincoln	4	1.15				0.01	9.49†						
	24	18.27				0.30	10.25						
	120	25.23				2.76	11.27						
Marquette	4										0.32		
	24										5.91		
	120										9.88		
Metal & Thermite	4								0.48	0.47†			0,01†
	24								4.45	2.71			0.34
	120								6.42	6.56			0.86
N.C.G.	4	3.54	0.66††		0.54					0.14†			
	24	8.16	4.56		6.20					4.43			
	120	13.34	11.53		10.97					7.83			
Westinghouse	4			0.90									
	24			7.02									
	120			9.40									

All electrodes are 5/32-inch diameter except:
† 3/16-inch, and †† 1/8-inch.

Moisture is reported as per cent of weight of dried coating.

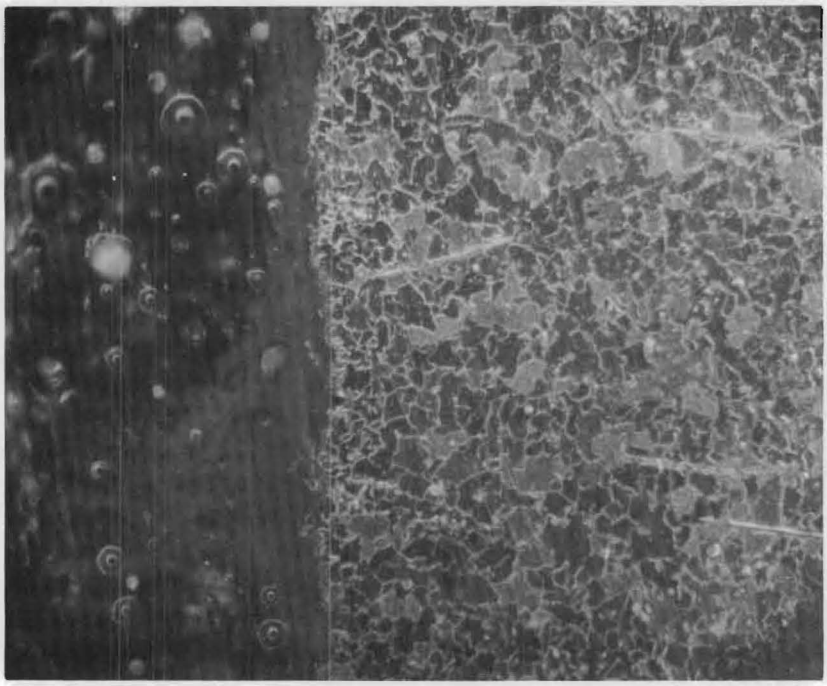

Figure 14. Enamel Metal Interface. (Metal is 3/16-inch C-1012 used in fabrication of T-joint specimens.)

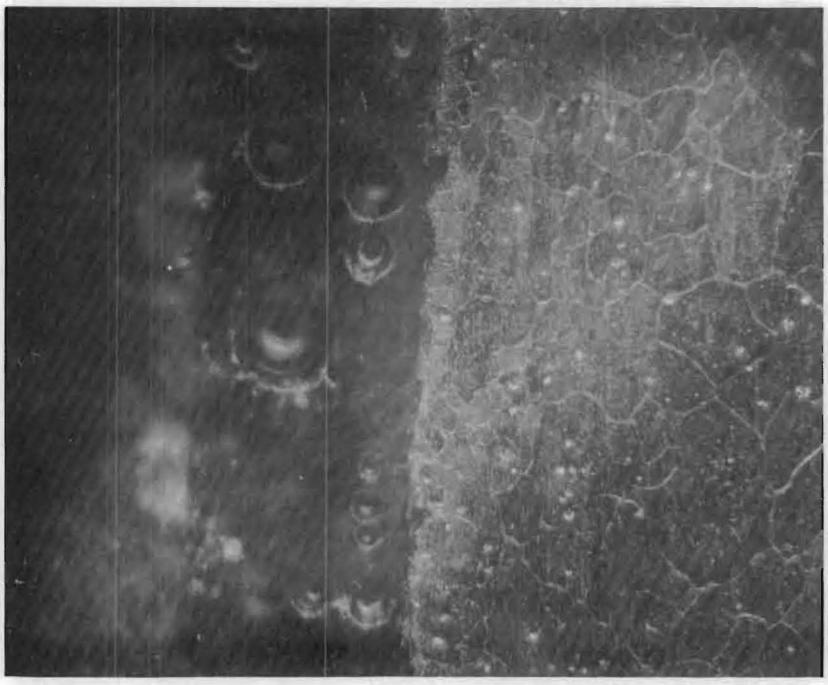

Figure 15. Enamel Metal Interface. (Metal is 3/16 inch capped steel. See Table I for steel composition.)

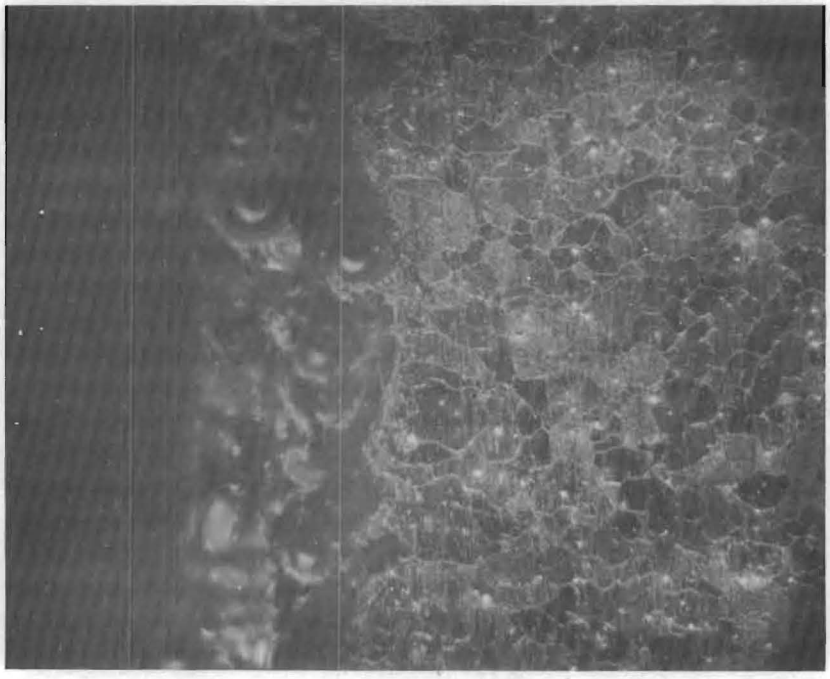

Figure 16. Enamel Metal Interface. (Metal is hot-rolled 0.17-inch rimmed steel. See Table I for steel composition.)

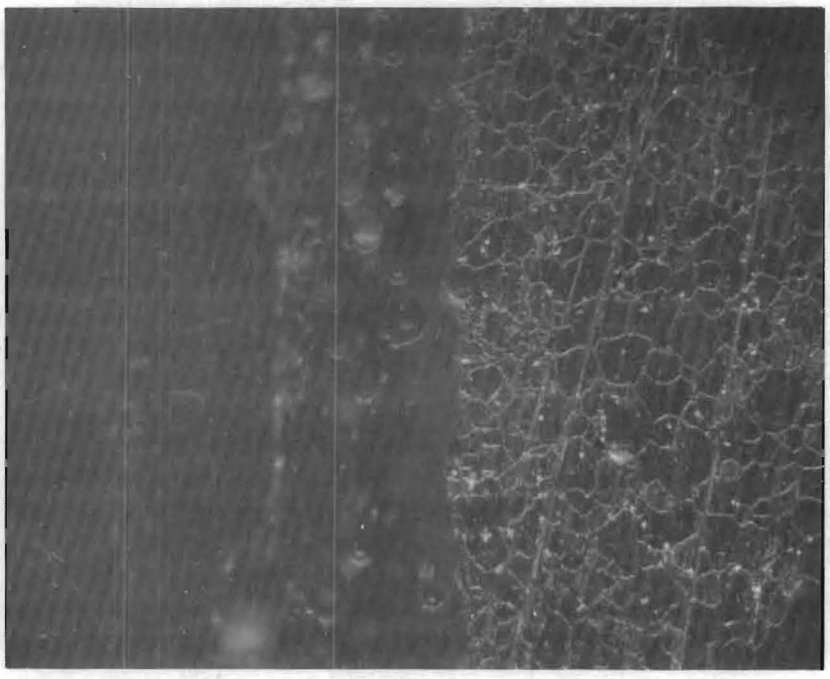

Figure 17. Enamel Metal Interface. (Metal is 0.126-inch rimmed steel after cold reduction of steel in Figure 16. See Table I for steel composition.)

Figure 18. Enamel Metal Interface. (Metal is Lukens T-1 plate 1/4" inch thick. See Table I for steel composition.)

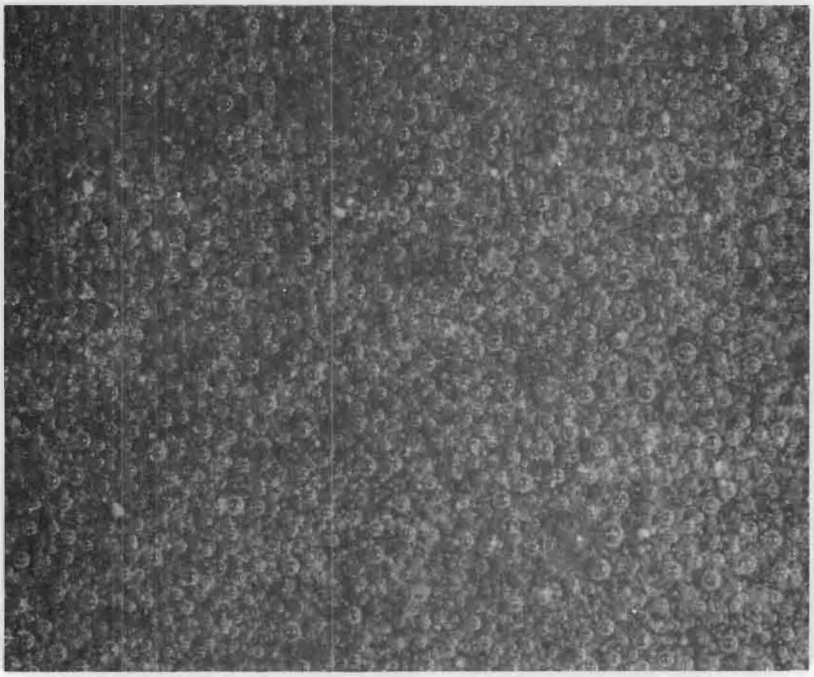

Figure 19. Bubble Structure of Recommended Enamel Fired for 10 Minutes.

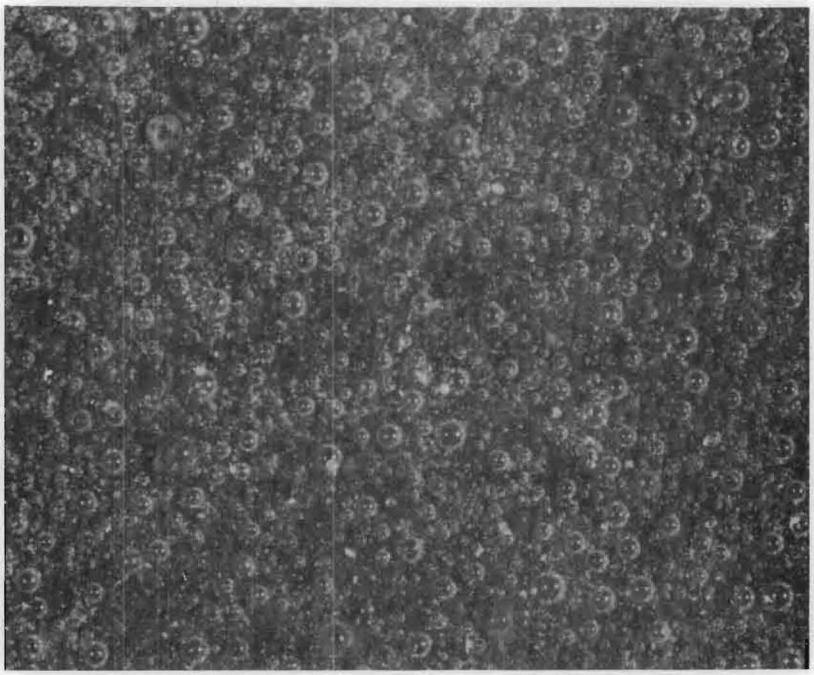

Figure 20. Bubble Structure of Recommended Enamel Fired for 15 Minutes.

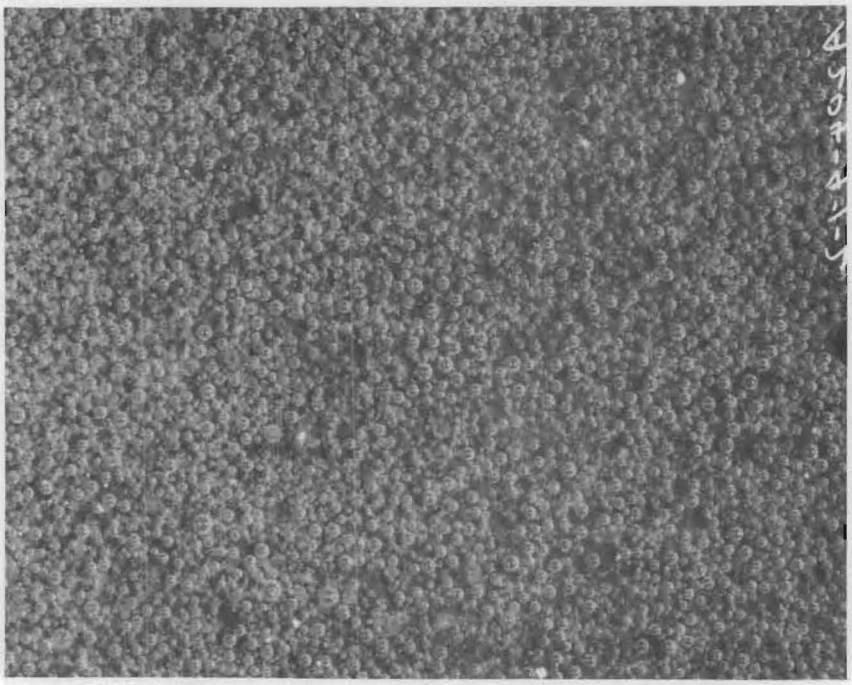

Figure 21. Bubble Structure of Enamel used as Basis for Developing Thermal Shock-Resistant Enamel.

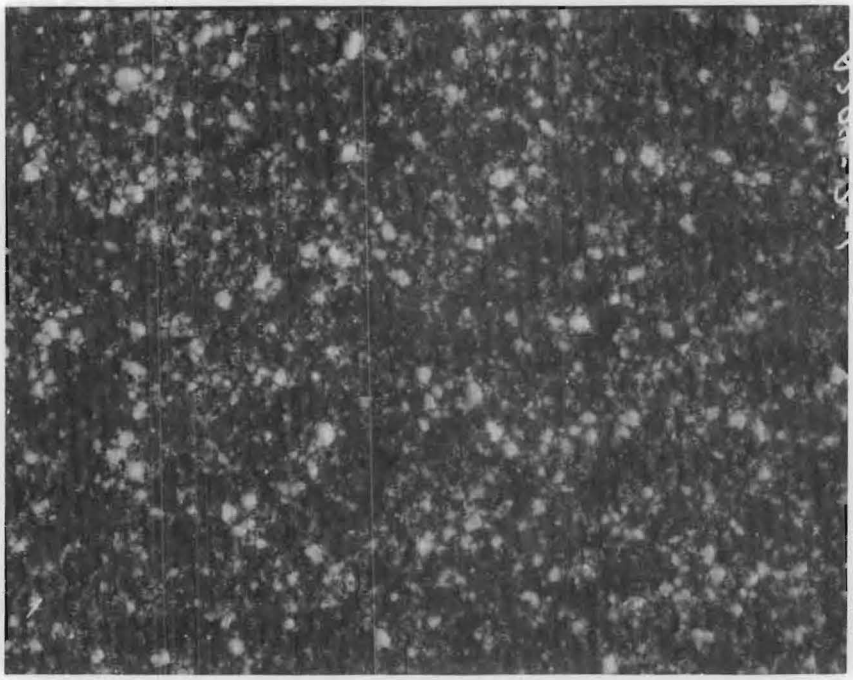

Figure 22. Bubble Structure of Enamel in Figure 21 with 10 Per Cent Alumina Added.

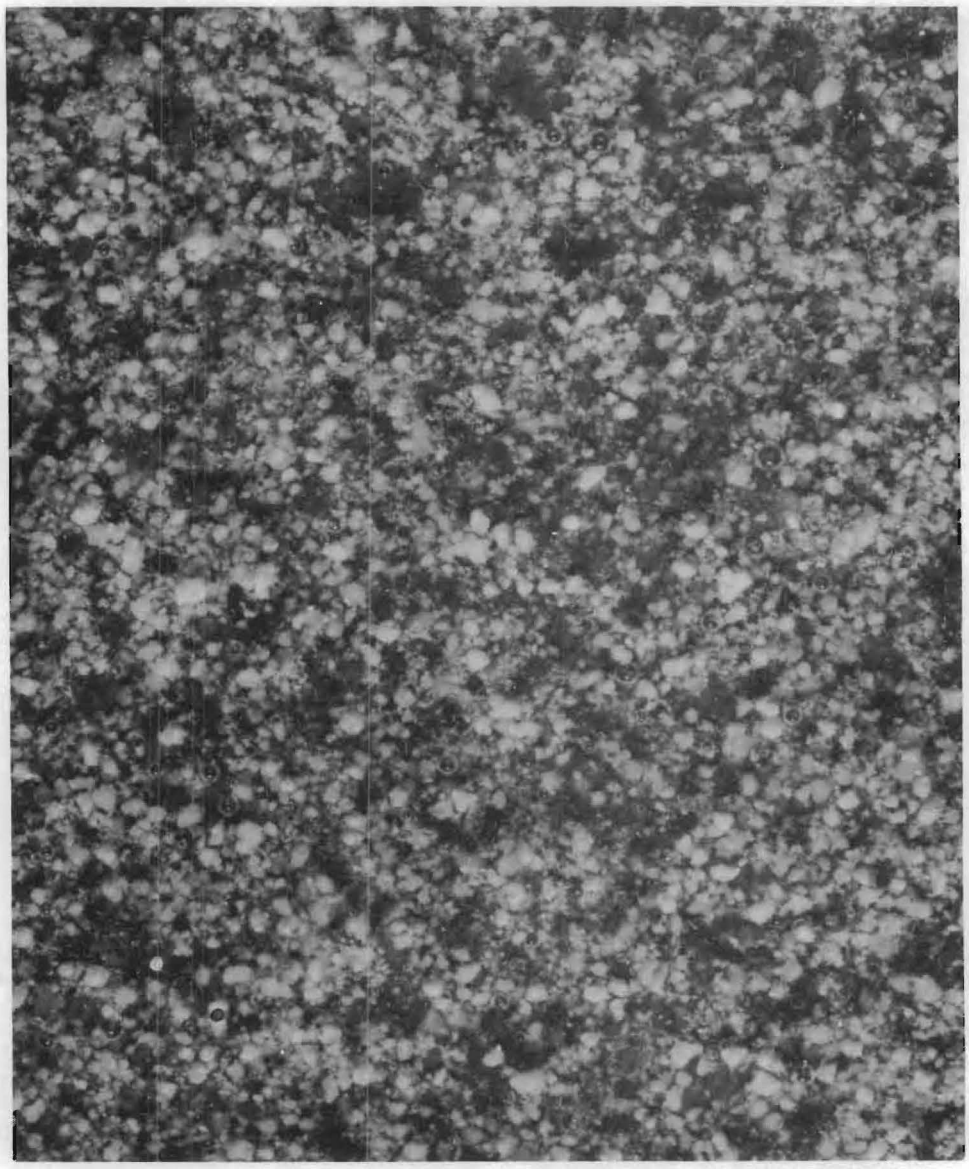

Figure 23. Bubble Structure of Enamel in Figure 21 with 20 Per Cent Alumina Added.

V. DISCUSSION

A. T-Joint Thermal-Shock Test

Throughout the work on passing the thermal shock test of MIL-P-16961B, it has been observed that all difficulty both from the standpoint of fish scale and from thermal-shock resistance has been with the 3/16-inch sections. In constrast to this, the 5/8-inch section has presented effectively no trouble. Likewise, the welded areas on the T-joint specimens have been noticeably free of defects.

Judging from these observations, it would appear that it is not necessary to construct a T-joint specimen in order to evaluate the enamelability of the steel itself. Perhaps a 4- by 8-inch sample from each lot of each thickness of steel to be used might be enameled and thermal shocked (according to the specifications of MIL-P-16961B) as a means of determining the suitability of the steel for such applications.

Any such test would of necessity be valid only for the enamel batch with which the steel was coated. Differences in the enamel used were very dramatic in the case where thermal-shock resistance ranged from poor, with a presumably good coating, to excellent on the same steel plate.

Of further interest were the results obtained when each ground coat was covered with a desired acid-resistant-cover coat. The thermal shock resistance, as would be expected, was dependent upon the ground-coat enamel, to the extent that over a ground coat which failed, the composite failed. In the other cases, it appeared that the cover-coat enamel may have failed, as evidenced by the crazing observed. However, the bond between the cover coat and ground coat was evidently of sufficient strength to hold the cover coat in place. This new

ground-coat enamel would, therefore, serve as a good base upon which to develop good thermal-shock-resistant cover-coat enamels.

B. Hydrogen Studies

The hydrogen diffusion test provided data of such poor reproducibility and questionable worth that it was abandoned in favor of the hydrogen extraction test.

In light of the results of the work to date, it appears that the frit and the firing atmosphere are the primary contributing factors to inducing hydrogen into steel.

First, it appears that moisture in the atmosphere does not contribute significant amounts of hydrogen into steel through the reaction of

$$H_2O + Fe \rightarrow FeO + H_2 \qquad (1)$$

since the amount of such hydrogen was insignificant except in the presence of actual flowing water.

Second, the equilibrium data reveal that the amount of atomic hydrogen produced through the dissociation of molecular hydrogen at firing temperatures is infinitesimally small even in an atmosphere of pure hydrogen gas. Thus it appears that the moisture in the atmosphere must contribute its influence as H_2O.

In considering moisture in the frit, however, a more available source of atomic hydrogen comes to light.

First, the presence of moisture at the interface is in direct contact with the metal. Thus, a greater chance for hydrogen to result from the reaction shown in formula 1 exists.

Second, one of the mechanisms by which adherence is achieved is the electrochemical replacement of cobalt from glass solution with iron being taken into solution. This reaction would promote the electrolysis of water at the areas in which this cell action was active, creating atomic hydrogen. Both of these mechanisms have been suggested by Moore et al. (6).

If these actions are responsible for the majority of hydrogen injected into steel during the firing operation, the amount of hydrogen would then be proportional to the amount of water present in the frit in equilibrium with the moisture in the furnace atmosphere.

With respect to means of preventing fish scale, it would appear that elimination of moisture from the frit and the atmosphere would prove the most successful remedy. However, this is not easily accomplished in practice, thus other means would seem desirable. One such method is evident from the hydrogen diffusion studies, and this is the cold working of the metal surface prior to coating (4, 7, 8). This cold worked surface provides areas of metal discontinuities at broken grain boundaries. These areas do not tend to stop the passage of atomic hydrogen being injected into the steel during the firing operation. However, upon the diffusion of hydrogen from the steel at room temperatures, molecular hydrogen is formed in the voids or areas of discontinuities and further diffusion is stopped. If the hydrogen can thus be prevented from entering voids produced at the enamel-metal interface resulting from undissolved oxide or poor wetting of the metal surface, fish scaling can be reduced. Other remedies such as improved bubble structure (1, 4) to better distribute the diffused hydrogen pressure over large areas may be considered.

C. Steel Variables

1. Hydrogen Extraction Data

From Table I it can be seen that no apparent correlation exists between the tendency to fish scale, or chemical composition, and the amount of hydrogen extracted. In the case of the hot- and cold-rolled rimmed steel, the amount of hydrogen extracted as related to thickness was reversed from that obtained when thickness alone was studied (see Figure 11). From this it would appear that some unknown factor was keeping the coating from fish scaling, since the cold-worked condition of the surface of the steel did not appear to prevent hydrogen from escaping from the steel.

From Figures 8 and 11, it can be seen that thickness, amount of moisture in the furnace atmosphere and firing time were important in determining the amount of hydrogen injected into steel.

The curves representing hydrogen extracted as a function of steel thickness suggest two things. First, the amount of hydrogen is a linear function of thickness, and, second, the surface of the steel itself is an important factor in the injection of hydrogen into the steel. The specimens representing points A, B and C were obtained by reducing the thickness of specimen F through machining off the surface. Specimens D, E and F were received as hot-rolled strips. The displacement of curve A-C from D-F would, therefore, appear to be due to the difference in the surface the specimens used. All specimens were sandblasted prior to enameling.

The variable of time appears to be important only to a point. If we assume that most of hydrogen injected into the steel results from the reaction between the glass and the steel, then the greatest change in the rate of reaction would

occur in the early stages of firing. This is indicated by the time curve of Figure 8.

The curve representing the effect of moisture content of the furnace atmosphere was as expected. The temperature scale represented the temperature of the water through which the air entering the furnace was passed.

In Figure 10, it was noted that exposure time had the greatest effect on hydrogen diffusion and shot velocity the least effect. Shot size did not produce too well-defined data. It is possible that a maximum degree of resistance to hydrogen diffusion was obtained at a shot size of S-170-WSS. However, with no further data to substantiate this possibility, a straight-line curve was used to depict the effect of this variable.

The effect of sodium hydride pickling on the amount of hydrogen extracted, with and without sandblasting is shown in Figure 9. Both curves indicate that the time immersed in the sodium hydride pickle decreased the amount of hydrogen extracted from the steel. Sandblasting, however, increased the amount of extracted hydrogen. This should not be taken necessarily as a detrimental effect. It is very probable rather that this indicated a greater degree of reactivity between the steel and the glass.

2. Fish Scale

In all cases where possible, 4- by 4-inch plates of each of the steels on which hydrogen-extraction data were obtained were coated under the same conditions, and the degree of fish scaling was observed.

With the exception of curve A-C and D-F, all the steel specimens used to obtain the data for Figure 1 were prepared as described previously. The range of firing time investigated had little effect on the fish scaling of the samples. All specimens exhibited this defect to a considerable degree. In the case of

varying the saturation temperature of air entering the furnace, fish scaling did not appear until the temperature of the water reached 30° C, and then only two fish scales appeared on a 4- by 4-inch plate. The fish scaling increased in severity as the saturation temperature increased beyond 30° C.

All of the shot-peened samples exhibited severe fish scaling. However, many of the fish scales exposed clean metal below. This would appear to indicate that poor adherence was developed between the glass and the steel. This was further evidenced when the 1-1/2- by 2-inch specimen was quenched after enameling, causing a large portion of the coating to spall from the section. Thus, although the extractable hydrogen varied somewhat because of shot-peening, the degree of adherence appeared to be below a level at which the coating could resist fish scaling.

This was further evidenced in the case of the sodium hydride pickled specimens. The samples coated "as received" spalled badly upon quenching. However, the hydride pickle followed by sandblasting provided a surface to which the glass adhered very well and did not spall when quenched. Likewise, after sandblasting, the extractable hydrogen increased almost 30 per cent over that obtained when the specimen was not sandblasted prior to enameling. In this instance all plates, sandblasted or not, exhibited slight fish scaling. It might appear possible that, in this case, the improved adherence merely increased at a rate comparable to the increased hydrogen produced, with the net resistance to fish scaling remaining constant.

D. Adherence

Very little work has been done on the adherence test to this time. The data reported in Table II represent tests run on only four samples. These data

indicate, however, that the test is sensitive to firing time. From Figure 13 it can be seen that at 3 per cent elongation considerable enamel remains on the strip. This particular strip was coated with only 3 mils of coating. A similar strip coated with 5 mils was more completely removed from the steel after a 3 per cent elongation. However, after elongating the strip 6 per cent, the thickness of coating had little effect on the results obtained.

Figure 13 shows very clearly the Luder's lines which follow lines of strain when low-carbon steel is stressed as in this adherence test. These lines make reproducibility much more difficult. However, as higher carbon steels are studied, these lines should become less evident.

E. Welding

The data reported in Table III indicate that quite a difference exists between the moisture absortive properties of the coatings of electrodes used for welding mild steels. It is anticipated that differences will likewise be found in the amount of hydrogen injected into the steel when these electrodes are used for welding after exposure to 100 per cent relative humidity for a period of 120 hours.

The electrodes which are indicated in Table III as being of a diameter other than 5/32-inch will be used as 5/32-inch diameter electrodes when the actual hydrogen studies are carried out. For the purpose of determining moisture pickup on the basis of moisture as a per cent of the weight of coating, the diameter of the rod was considered to be unimportant.

F. Photomicrographs

The photomicrographs shown in Figures 14-18 indicated no significant differences in the appearance of the interfaces of the enamel and the five

types of steel used. In all instances there was a "muddy" area directly adjacent to the steel and extending into the enamel. This appeared to be iron oxide.

In Figures 19-23 considerable differences were evident between the two enamels used, as well as between the two firing periods studied. The bubbles became fewer and larger as firing time increased in Figures 19 and 20. However, the enamels in Figures 21-23 were fired for 15 minutes but exhibited much smaller bubbles. In Figure 22 it can be seen that the bubbles remained small and the number decreased over Figure 21. Much more of the "muddy" appearance was likewise evidenced in the enamel used in Figures 21-23 as compared to the other enamel of Figures 19 and 20. In Figure 23 the aluminum oxide almost completely covered the muddy area and the number of bubbles was decreased much more.

From this study it would appear that the size of the bubbles was an important factor in obtaining thermal-shock resistance.

VI. FUTURE WORK

Work planned for the immediate futute has been divided into the following categories:

A. Materials

1. Plate

a. Hot rolled steel plates, 9 inches long and full width cuts from 3/16-inch stock have been received with the following carbon content: 0.07, 0.13, 0.14, 0.15, 0.19, 0.24, 0.27, 0.36 and 0.44.

b. Cold and hot reduction of AISI C-1012 plate is being carried out from one piece of stock in order to study thickness and method of reducing steel.

c. Steel has been requested, AISI, C-1010 grade, semi-killed and fully killed, by both silicon and aluminum.

2. Weldments

The welding electrodes which have been reviewed will be used with the coating in the dry and moist condition to butt weld strips 1 by 3/16 - by 14-inches and 1 by 3/16- by 12-inches long.

B. Tests

1. Hydrogen Extraction

Hydrogen extraction data will be obtained on all of the steels of VI ,A,1 after enameling, as well as from a portion of the 12-inch strip welded by each electrode in VI ,A, 2 before enameling.

2. Fish Scaling

Tendency to fish scale in all conditions studied in chapter VI, A, 1, b will be recorded.

3. Adherence

The adherence test will be run on all specimens of VI, A.

4. Wetability

The wetability of all samples will be determined by observing the contact angle between an enamel pellet and the surface of each specimen after the enamel has been allowed to fuse. These data will be determined in normal and inert atmosphere.

5. Oxidation

The oxidation tendency of all specimens of VI, A will be determined by recording the weight change of the specimen as a function of time at firing temperature.

6. Surface Tension

Equipment is being constructed to measure the surface tension of glass. The effect of iron oxide on the surface tension of the enamel used in these studies will be determined.

7. Spectrograph

Spark spectrographic analyses of all welded specimens will be carried out in order to determine the arc transfer efficiency as well as the actual composition of the welded area to be coated.

C. Correlation

A correlation will be attempted between the results of the tests described

above and the physical and chemical properties of the plates and weldments studied.

Respectfully submitted:

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